

Solar Silicon via the Dow Corning Process

(NASA-CR-163798) SOLAR SILICON VIA THE DOW
CORNING PROCESS Final Report (Dow Corning
Corp.) 106 p HC A06/MF A01 CSCL 10A

N81-12551

Unclas
29409

G3/44

FINAL REPORT

October 1979

L. P. HUNT and V. D. DOSAJ

DOW CORNING CORPORATION

Solid-State Research and Development Laboratory
Hemlock, Michigan 48626

JPL Contract NO. 954559

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

DOW CORNING

DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640



Solar Silicon via the Dow Corning Process

FINAL REPORT

October 1979

L. P. HUNT and V. D. DOSAJ

DOW CORNING CORPORATION

**Solid-State Research and Development Laboratory
Hemlock, Michigan 48626**

JPL Contract NO. 954559

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

DOW CORNING

DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640

ABSTRACT

The process developed under this contract meets the LSA Project objective of demonstrating technical feasibility for high-volume production of solar cell-grade silicon. The process consists of producing silicon from pure raw materials via the carbothermic reduction of quartz. This silicon was then purified to solar grade by impurity segregation during Czochralski crystal growth. Commercially available raw materials were used to produce 100-kg quantities of silicon during 60-hour periods in a Direct Arc Reactor. This silicon had impurity concentrations of less than 10 ppmw each, except for Al and Fe (50-100 ppmw). Purification of this material by Czochralski crystal growth gave silicon of semiconductor purity, except for Al (1 ppma), B (7 ppma, 0.1 ohm-cm), and P (0.5 ppma). This silicon produced single crystalline ingot, during a second Czochralski pull, that was fabricated into solar cells having AM1 efficiencies ranging from 8.2% to greater than 14% (AR-coated). An energy analysis of the entire process indicated a 5-month payback time. A price of \$12.15 (1980 dollars, with profit) was estimated for a 3000-metric-ton-per-year plant. Further process development is recommended based upon technical success, estimated product cost, and commercially-available technology already existing in the industry that can be applied to process scale-up.

PRECEDING PAGE BLANK NOT FILMED

TABLE OF CONTENTS

Page No.

Abstract	iii
Table of Contents	v
List of Tables	vii
List of Figures	ix
List of Appendices	x
I. Summary	1
II. Introduction	4
III. Impurity Analyses	7
IV. Raw Materials	10
A. Summary	10
B. Purity Requirements	10
C. Silica	18
1. General Survey	18
2. Quartz Compositional Analysis	18
3. Decrepitation of Quartz and Quartzites	21
4. Quartz Sand	22
D. Carbon	25
1. Reductants	25
a. General	25
b. Carbon Black and Activated Carbon	25
i. As-received Material	25
ii. Pellets	28
c. Other Reductants	32
i. Charcoal	32
ii. Lignite	34
iii. Petroleum Coke	34
iv. Sugar Char	35
2. Electrode	35
V. Silicon Production Step	37
A. Summary	37
B. Experimental	37
1. General	37
2. Charcoal as Reductant	41
3. Carbon Black and Activated Carbon as Reductants	43

PRECEDING PAGE BLANK NOT FILMED

TABLE OF CONTENTS (cont.)

	Page No.
VI. Silicon Purification Step	51
A. Summary	51
B. Czochralski Crystal Growth	52
1. Impurity Segregation during Growth of Poly-Silicon	52
2. Poly-Ingot Compositional Analysis	55
a. Boron and Phosphorus	55
b. Other Impurities	58
3. Poly-Ingot Yield	60
C. Bridgman Crystal Growth	63
1. Experimental	63
2. Cost Analysis	70
3. Conclusions	70
D. Vacuum Evaporation	71
1. Background	71
2. Experimental Procedure	71
3. Results	71
VII. Evaluation of SoG-Si as Solar Cells	74
VIII. The Dow Corning Process	76
A. Preliminary Process Flow Diagram	76
B. Preliminary Cost Analysis	76
C. Energy Analysis	82
IX. Conclusions	85
X. Recommendations	87
XI. References	89
XII. Acknowledgements	91
XIII. Appendices	92

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
1	Calculated Maximum Impurity Concentrations in DAR-Si from Assumed Impurity Concentrations in SOG-Si	12
2	Calculated Maximum Impurities in Raw Materials from Impurities in DAR-Si	16
3	Comparison of Impurity Concentrations in MG-Si to the Goal for DAR-Si	17
4	Some Foreign and Domestic Sources of High-Purity Silica	19
5	Average Analyses of Various Quartz Samples Abstracted from Appendix A	20
6	Decrepitation Characteristics of Various Quartz Samples	23
7	Analyses of Carbon Reductants Used to Commercially Produce MG-Si	26
8	Average Analyses of Activated Carbon Samples that Meet Purity Goals	27
9	Average Analyses of Carbon Black Samples	29
10	Average Analyses of Binders to Produce Pellets	30
11	Average Analyses of Carbon Black and Activated Carbon Pellets Used in DAR Experiments	31
12	Charcoal Purification by Fluorocarbon Treatment	33
13	Analysis of a Purified 15-cm-Diameter Electrode	36
14	Data for Silicon Production Using Charcoal as a Reductant	42
15	Analyses of Silicon Produced Using Charcoal as a Reductant in DAR-50	44
16	Analyses of Silicon Produced Using Charcoal as a Reductant in DAR-200	45
17	Data for Silicon Production Using Activated Carbon and Carbon Black Reductants	47

LIST OF TABLES (cont.)

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
18	Summary of Silicon Production Experiments Detailed in Table 17	48
19	Analysis of Silicon Produced Using Activated Carbon and Carbon Black as Reductants in DAR-200	49
20	Comparison of Purification by Czochralski Freezing of Single-Crystal and Polycrystalline Silicon Ingots	54
21	Boron and Phosphorus Analyses of the Final SoG-Si Product from the Dow Corning Process as Pulled from Various DAR-Si Melts	57
22	Analysis of SoG-Si Ingot for Impurities Other than Boron and Phosphorus	59
23	Yield of SoG-Si Poly-Ingot from DAR-Si Using Czochralski Purification	61
24	Bridgman-Type Experiments to Segregate Impurities during Unidirectional Solidification	65
25	Impurity Analyses of Silicon Subjected to Vacuum Evaporation for Various Time Periods	72
26	Solar Cell Data from Applied Solar Energy Corporation for cells Fabricated from Wafers Cut from a Czochralski Ingot Pulled from SoG-Si (DAR-200-17).	75

LIST OF FIGURES

<u>Fig. No.</u>	<u>TITLE</u>	<u>Page No.</u>
1	Schematic Diagram of the Dow Corning Process for Producing SoG-Si	5
2	Impurity Recovery as a Function of Elemental Vapor Pressure at 1650 °C	14
3	Dimensions and Construction of DAR-50	38
4	Cross-Sectional View of the DAR after Successful Silicon Smelting	40
5	Schematic of Silicon Processing during Czochralski Crystal Growth Studies	53
6	Gradient Furnace Schematic	64
7	Photograph of Grain Structure in Bridgman-Solidified Silicon Ingot (Scale in mm)	67
8	Effect of Segregation on Aluminum Concentration During Bridgman-Type Solidification	69
9	Preliminary Process Flow Diagram for a 3000-Metric-Ton-Per-Year Solar Silicon Plant	77
10	Estimated Installed Capital (1975 Dollars) for Producing 3000 MT/y of SoG-Si Via the Dow Corning Process	79
11	Total Estimated Cost (1975 Dollars, no Profit) of SoG-Si for Producing 3000 MT/y Via the Dow Corning Process	80
12	Variation of SoG-Si Cost (1975 Dollars and no Profit) with Ingot Diameter and Silicon Yield	81
13	Total Estimated Cost (1975 Dollars, no Profit) for Producing 3300 MT/y of DAR-Si	83
14	Total Estimated Cost (1975 Dollars, no Profit) for Producing 3000 MT/y of SoG-Si from a DAR-Si Plant	84

LIST OF APPENDICES

<u>Appendix No.</u>	<u>Title</u>	<u>Page No.</u>
A1	Impurity Analyses of Arkansas Clear Quartz	93
A2	Impurity Analyses of Arkansas Semi-Clear Quartz	94
A3	Impurity Analyses of Arkansas Milky Quartz	95
A4	Impurity Analyses of British Columbia Quartz	96
B	Analyses of Activated Carbon Samples that Do Not Meet Purity Goals	97
C	Cross Reference of Carbon Black Sample Numbers with Suppliers of Materials	98

I. SUMMARY

The process developed under this contract meets the Phase-I objective of the Silicon Materials Task of the Low-Cost Solar Array Project: to demonstrate the technical feasibility of a process capable of high-volume production of solar-cell-grade silicon. Work was performed during the period from July 31, 1976 through October 31, 1978.

The Dow Corning Process consists of producing silicon via the carbothermic reduction of quartz utilizing high-purity raw materials. This silicon is subsequently purified to solar-grade silicon by pulling a polycrystalline ingot via the Czochralski process.

Commercial sources of raw materials were identified that meet the requirements of price, chemical reactivity, and possibly purity. These sources resulted from a broad survey of silica and carbon materials. The purest silicon attainable was produced from quartz, mined from both United States' and Canadian deposits, and carbon black/sucrose pellets. A reliable analytical technique must yet be developed to provide quality assurance of the raw materials.

Stable and continuous silicon production was demonstrated in a 200-kVA Direct Arc Reactor to produce quantities of silicon in excess of 100 kg per experiment. A production rate as high as 3 kg/h was accomplished at an energy consumption as low as 26 kWh/kg Si. The silicon analyzed to be relatively pure, having concentrations of 50-100 ppmw for aluminum and iron and of less than 10 ppmw each for other impurities. Based on commercial experience no major scale-up problems are envisioned for this process step. However, more sophisticated handling of raw materials should be developed.

Purification of Direct-Arc-Reactor silicon to solar-grade quality was explored using crystal growth and vacuum evaporation. No reduction in the concentration of any

impurity could be detected using vacuum evaporation. Segregation of impurities during ingot production using Bridgman-type crystal growth was demonstrated to be feasible. However, it was not pursued in depth due to the greater degree of technical sophistication of Czochralski crystal-growth technology.

Purification of Direct-Arc-Reactor silicon to solar-grade quality was demonstrated to be possible using Czochralski crystal growth to produce a polycrystalline ingot during the last experiment performed under this contract. Impurity segregation was as effective as single-crystal growth from semiconductor silicon since the melt was dilute enough to prevent constitutional supercooling. Analysis of the polycrystalline silicon ingot showed the final product to be of semiconductor purity except for Al (1 ppma), B (7 ppma, 0.1 ohm-cm), and P (0.5 ppma).

Single-crystal silicon was produced from the polycrystalline ingot using a second Czochralski crystal-growth operation. This single-crystalline material was fabricated into solar cells that demonstrated conversion efficiencies ranging from 8.2% to greater than 14% (AM1, AR-Coated) depending upon the fabricator and the cell fabrication technique. More detailed solar cell evaluations should be performed.

A cost analysis of the Dow Corning Process at a 3000-MT/y rate, in 1975 dollars with no profit, showed that the estimated cost of silicon from the Direct Arc Reactor to be \$2.28/kg. Final solar-grade silicon cost is dependent upon the cost assumptions made from Czochralski growth. A final cost of \$7.54/kg is possible if 30-cm-diameter ingots can be pulled continuously with 90-% yield. Today's crystal growth technology would allow a final cost of \$11.70/kg when pulling a 15-cm-diameter ingot at an 80-% yield.

A complete energy analysis of the Dow Corning Process from raw materials through solar-grade silicon product indicates that only a 5-month period is required to pay back the energy consumed in the overall process. A 12-% AM1 cell was assumed to be exposed for 5 hours each day to a solar flux of 100 mW/cm². Calculations were made for a 100-cm-diameter by 200-μm-thick cell (3.6g Si).

In the opinion of the Dow Corning Corporation, further development of the Dow Corning Process should continue based upon the demonstrated technical success, the low-cost potential for the final product, and the commercially-available technology already existing in industry that can be directly applied to scale-up of the two process steps.

II. Introduction

This report covers technical effort performed under JPL contract during the period from July 31, 1976 through October 31, 1978. The contract work was carried out under Phase I of Part III of the Silicon Material Task of JPL's Low-Cost Solar Array (LSA) Project.

The LSA Project objective is to "develop national capability to produce low-cost, long-life photovoltaic arrays at a rate greater than 500 MW/y and at a price less than $\$500/\text{kW}_p^*$ by 1986 with array performance goals of $>10\%$ efficiency and $>20\text{-y}$ operating lifetime". (1). The long-term objective of the Silicon Materials Task is to "establish installed plant capability for producing silicon suitable for solar cells at a price less than $\$10/\text{kg}^*$ at a rate equivalent to $\$500/\text{kW}_p$ " (1).

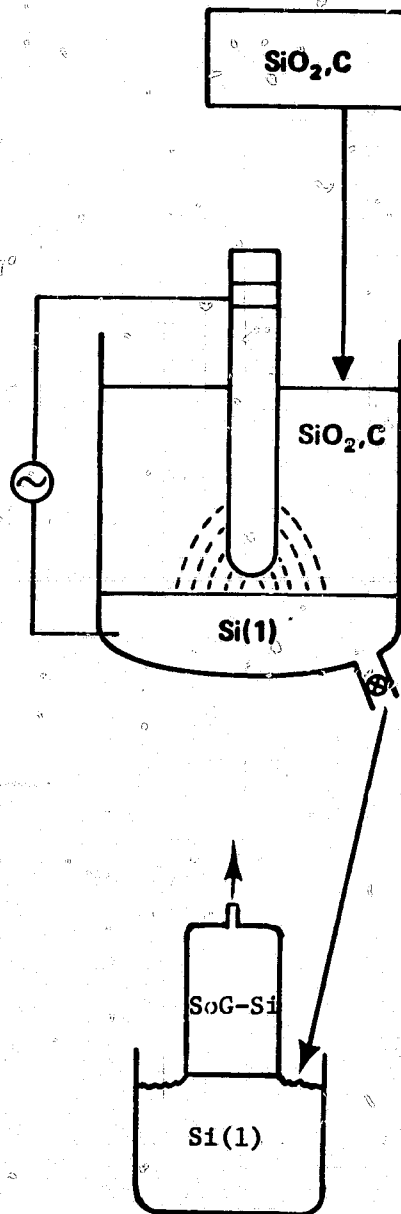
The past 27-month effort has been directed at meeting the short-term objective of the Phase-I/Part-III portion of the Silicon Materials Task: "to establish the technical feasibility and practicality of a process capable of high-volume production of solar-cell-grade silicon" (1).

Dow Corning's approach to meeting the above objective has been to develop and interface two major process steps: a chemical process step of reducing silica to silicon, with carbon as the reductant, followed by a physical process step of purification by means of impurity segregation during solidification of the molten silicon. This basic concept is shown schematically in Figure 1.

A major advantage in the Dow Corning approach is that the basic technology exists today for carrying out each process step. Silicon of 98-% purity is commercially produced in 20,000-metric-ton-per-year electric arc furnaces.

* In 1975 dollars

PROGRAM TASKS



A. Quartz and Carbon Raw Materials

B. Silicon Production via the Reaction $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$

C. Silicon Purification via Unidirectional Solidification

Figure 1. Schematic Diagram of the Dow Corning Process for Producing SoG-Si.

This compares to the estimated SoG-Si requirement in 1986 of only 3000-6000 MT/y*. The problem to be solved in this process step is to produce silicon of greater than 98-~~9~~ purity by reacting high-purity raw materials in a noncontaminating reactor. It is imperative to maintain the concentrations of boron and phosphorus at low levels during this process step since neither impurity is efficiently removed during the subsequent purification step.

Fundamental technology also exists for the silicon purification step of segregating impurities during unidirectional solidification. The semiconductor industry routinely converts polycrystalline semiconductor silicon to single crystalline ingots using Czochralski technology. The major problem in applying this technology is to engineer larger-capacity equipment for providing higher throughput economy.

The remainder of this report describes Dow Corning's approach and progress in attempting to solve the problems of silicon production and purification. It starts with a discussion of the capabilities and limitations of analytical techniques for analyzing impurities in silicon, quartz, and carbon sources. After describing the various options for raw materials and for silicon production and purification techniques, the report provides a description of the selected Dow Corning Process in terms of the process flow diagram and cost and energy analyses.

* MT = Metric Ton

III. IMPURITY ANALYSES

Successful commercialization of a product depends upon codevelopment of the process along with the product. Product introduction to a market is useless if there is not a good process by which to produce it. Conversely, a process is of no utility if its product does not meet the requirements of the market place. It is this last item that this section addresses itself: how does one analyze the product to determine whether it is any good? More precisely, how can silicon--or the materials used to produce it--be sufficiently analyzed to determine its suitability for being fabricated into a solar cell array?

The most obvious method of evaluating silicon as a photovoltaic device is to fabricate solar cells from it and to evaluate their electrical parameters. Not having facilities to do this, we have had solar cell companies perform this evaluation for us.

Compositional analysis of silicon is important in order to determine what impurity, if any, might be limiting solar cell efficiency. Compositional analysis of raw materials is also important since impurities must have certain minimum concentrations as determined by their carry-through yields in the various process steps. Therefore, it is necessary to be able to analytically evaluate silicon, carbon, and silica (quartz). The ideal technique should be accurate, precise, fast, low cost, and highly sensitive for impurities of interest. No such technique exists, however, to analyze the materials having the high purity required for solar-grade silicon.

Examination of the following section on "Raw Materials" shows that impurities in SoG-Si must be below the range of about 0.1 ppbw-1 ppmw in order to produce solar cells with high conversion efficiencies. The raw materials required in the Dow Corning Process, then, must have maximum acceptable impurity levels in approximately the range of 1-1000 ppmw.

We have typically analyzed 13 elements, as seen later in the report. These consist of mainly doping elements (Al, B, and P) and heavy metals that can severely degrade solar-cell performance even at low concentrations (e.g., Ti, V, and Zr). The following elements have been looked for by emission spectroscopy but never detected in even relatively impure materials such as MG-Si and charcoal:

- <5 ppmw: Ag
- <10 ppmw: Be, Bi, Co, Ge, In, Sn
- <50 ppmw: Cd, Sb, Sr, Zn
- <100 ppmw: As, Nb, W

Since over 600 samples were analyzed during the course of this contract, emission spectroscopy was used to analyze most samples. This service was performed by National Spectroscopic Laboratories, Inc. of Cleveland, Ohio. In general, a 13-element scan was provided for \$92.50 per sample. The limits of detection were either 5 or 10 ppmw for all elements. Boron and phosphorus could be measured to 1 ppmw using chemical concentration techniques. Boron determination in carbon samples was even more sensitive (0.2 ppmw) using chemical concentration. Phosphorus, which can only be measured down to about 0.5% by emission spectroscopy, was actually determined by a wet chemical colorimetric procedure at NSL.

Spark-source mass spectroscopy can measure impurities of interest down to the 1 to 100-ppbw range when a dedicated instrument is used, such as the one at Dow Corning. This specific instrument has, for the most part, seen only semiconductor-grade silicon and consequently has no "memory" for various impurities. Although both boron and phosphorus can be detected down to about the 10-ppbw level, their chemical concentration measures lower than the concentration calculated from resistivity measurements made on single crystalline material, especially in the area of about 1 ppmw.

Values reported for boron and phosphorus in this report are based on resistivity measurements. Silicon from the DAR is loaded into a Czochralski machine and a polycrystalline ingot is pulled. This ingot is multiply float zoned to produce a single crystalline silicon rod. Resistivity measurements are made on the first-pass section to yield a compensated boron value. The resistivity measurement on the seven-pass section yields an uncompensated boron value since phosphorus has segregated out. The difference in the two resistivities gives the phosphorus concentration. The concentrations are then corrected to give their actual values in the Czochralski ingot since this is the final product from the Dow Corning Process.

In summary then, several analytical techniques are used to evaluate raw materials and the silicon product. For the raw materials, emission spectroscopy, wet chemical, and spark-source mass spectroscopy are employed. SoG-Si is evaluated by these three techniques as well as by resistivity measurements. Final evaluation is performed by determining the efficiencies of fabricated solar cells.

IV. RAW MATERIALS

A. Summary

Determination of the yields of impurities in each process step allowed the maximum permissible concentration of impurities in the raw materials to be calculated from a definition of SoG-Si (see Table 1). Boron and phosphorus were shown to be the most critical impurities.

A survey of over 90 sources of silica indicated that quartz can possibly meet purity goals. This must be tested by determining boron and phosphorus in the silicon product due to the lack of reliable analytical techniques for measuring their concentrations in quartz. Two commercial sources of quartz were identified as meeting the requirements of cost and chemical reactivity.

Quartz sands still remain to be examined as potential sources of silica. cursory investigation shows that sands are available that meet purity and cost goals. These sands must be further pelletized and tested for reactivity.

Several carbon sources were examined as potential reductants: activated carbon, carbon black, wood and sugar charcoal, lignite, and petroleum coke. Only activated carbon and carbon black pellets meet the goals of high purity and high chemical reactivity. The latter goal is especially reached when activated carbon and carbon black are used in conjunction with sucrose either in the form of sugar cubes or as a binder for pellets.

B. Purity Requirements

It is necessary to establish the maximum allowable impurities in raw materials used for the Dow Corning Process since a specific degree of purification occurs for each element in the two process steps. The second process step of unidirection solidification is especially effective for

removing impurities because their distribution is orders-of-magnitude less in the solid phase as compared to the molten phase--except for boron ($\eta=0.8$) and phosphorus ($\eta=0.35$). Since relatively little purification occurs during the first process step of silicon production, raw materials must contain low concentrations of boron and phosphorus.

A method of determining the maximum concentration of impurities allowable in the raw materials is to start with the maximum allowable concentration in the solar grade silicon (SoG-Si) product and to calculate backwards to the raw materials using the yields of the impurities in both process steps. In doing this, various assumptions must be made that have an end effect on the final calculated concentrations. Therefore, the assumptions are discussed so that any later changes in them can be taken into consideration in terms of their effect on the calculated impurity requirements for the raw materials.

Two sources of information were used to help develop the maximum permissible impurity levels in SoG-Si. For boron, various data predict solar cell efficiency to peak between 0.1 ohm-cm (2-5) and about 0.3 ohm-cm (15,16) which corresponds to boron concentrations between 9.6 and 1.7 ppma, respectively. The maximum concentration of 1.7 ppma for boron was chosen so as to be conservative. An aluminum concentration of 0.2 ppma was chosen so as to be one order-of-magnitude lower than the other p-type dopant boron. Phosphorus was set at 0.5 ppma so as not to heavily compensate boron. The metal concentrations were obtained from Westinghouse-Dow Corning data (6) of relative cell efficiency versus impurity concentration; an efficiency 90 % of baseline was chosen. The various assumed impurity concentrations are summarized in Table 1.

Table 1 lists the calculated maximum concentrations of impurities that can be in silicon from the Direct Arc Reactor (DAR) assuming that DAR-Si of the given composition is converted to SoG-Si via the Czochralski technique of unidirectional

Table 1. Calculated Maximum Impurity Concentrations in DAR-Si from Assumed Impurity Concentrations in SoG-Si.

Impur- ity	SoG-Si	CZO	DAR-Si	
	Assumed SoG-Si Definition (ppma)	η^* CZO	Calc. ppma	Calc. ppmw
Al	0.2	2×10^{-3}	100	100
B	1.7	0.8	2	0.8
Cr	4×10^{-3}	1.1×10^{-5}	400	700
Cu	0.8	8×10^{-4}	1000	2000
Fe	6×10^{-3}	6.4×10^{-6}	900	2000
Mn	2×10^{-3}	1.3×10^{-5}	200	300
Ni	1	3.2×10^{-5}	30000	70000
P	0.50	0.35	1.4	1.6
Ti	6×10^{-5}	2.0×10^{-6}	30	50
V	8×10^{-5}	4×10^{-6}	20	40
Zr	2×10^{-4}	$< 1.5 \times 10^{-7}$	> 1000	> 4000

* Reference 6.

solidification. Impurity segregation coefficients between molten and solid silicon were taken from a recent Westinghouse report (6). Segregation coefficients are in effect the fractional impurity yields during the second process step. As an example of the calculation method, the maximum aluminum concentration of 0.2 ppma was divided by the aluminum segregation coefficient of 2×10^3 to obtain the 100 ppma maximum concentration in DAR-Si. An even higher concentration is most likely allowable since all aluminum in silicon is not electrically active from the standpoint of resistivity measurements.

The calculated maximum concentrations of Cu, Fe, Ni, and Zr are so high that they would cause supercooling of the melt and eventual breakdown of impurity segregation during Czochralski ingot growth resulting in low SoG-Si yield. It is assumed that a 90-% ingot yield will result if total metal concentration in the melt is kept less than 400 ppma. This assumption is based upon practical experience in pulling ingots from silicon having impurities varying between 2% (metallurgical grade) and sub-ppma (semiconductor grade) levels. Therefore, 400 ppma is used in Table 2 for the maximum permissible concentration of Cu, Fe, Ni and Zr in DAR-Si. This upper limit is also used for Ca and Mo since both have very favorable segregation coefficients--this assumes Ca is similar to Mg (6).

The revised maximum levels of impurities in DAR-Si were used to calculate their maximum levels in the raw materials by using impurity yields that occur during the first process step. These yields were measured by Interlake, Inc. over a 5-day period in a 30-MVA commercial arc furnace used to produce 98 % silicon at a rate of about 1 MT/h. The yields (recoveries) of the impurities in silicon are shown in Figure 2 and are seen to be inversely related to their elemental vapor pressures (7).

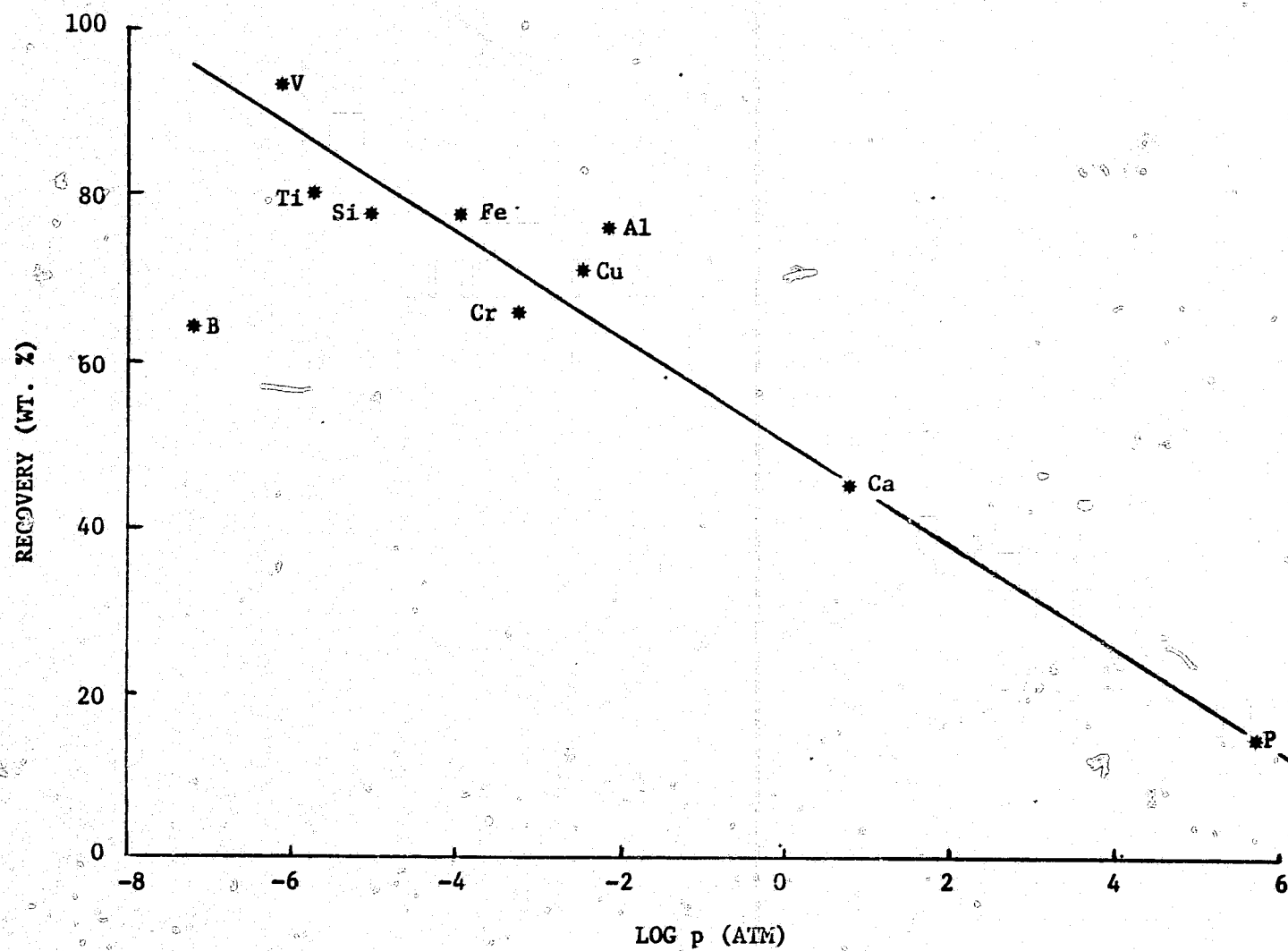


Figure 2. Impurity Recovery as a Function of Elemental Vapor Pressure at 1650 °C.

The maximum level of impurities in carbon and silica, as seen in Table 2, indicate that the impurities can be divided into three categories: (1) boron and phosphorus which must have concentrations in about the 1 to 10-ppma range, (2) aluminum, titanium, and vanadium which can be present in the 10 to 100-ppmw range, and (3) the remaining impurities that can range from 0.2 to 2 %. The requirement of having boron and phosphorus present at the low 1 to 10-ppmw level almost guarantees that the levels of all other impurities will fall considerably below their maximum allowable concentrations in the raw materials. This becomes obvious from the analysis of silica and carbon shown in later sections of this report.

The need to use higher-purity raw materials in the silicon production step can be recognized when comparing the impurity goals for DAR-Si to actual impurity analyzes of metallurgical-grade silicon (MG-Si). The comparison in Table 3 indicates that the concentration of Al, B, Fe, and P impurities in MG-Si are more than an order-of-magnitude higher than their concentration goals for DAR-Si.

Table 2. Calculated Maximum Impurities in Raw Materials from Impurities in DAR-Si.

Impurity	DAR-Si	DAR	SiO ₂	+2C
	Calc.* ppmw	η^{**} DAR	Calc. ppmw	Calc. ppmw
Al	100	0.80	60	100
B	0.8	0.66	1	1
Ca	600 ⁺⁺	0.50	600	1000
Cr	700	0.67	500	1000
Cu	900 ⁺⁺	0.73	600	1000
Fe	800 ⁺⁺	0.80	500	1000
Mn	300	0.60 ⁺	200	600
Mo	1400 ⁺⁺	1.0 ⁺	700	2000
Ni	800 ⁺⁺	0.82 ⁺	500	1000
P	1.6	0.14	5	10
Ti	50	0.82	30	70
V	40	0.95	20	50
Zr	1300 ⁺⁺	1.0 ⁺	600	1500

* See Table 1 and text.

** Reference 7.

+ Estimated from yield versus vapor pressure curve in Figure 2.

++ These ppmw values are equivalent to 400 ppma, each. However, it is noted that the total metal concentration should not exceed 400 ppma (see p.13).

Table 3. Comparison of Impurity Concentrations in MG-Si to the Goal for DAR-Si.

Impurity (ppmw)	DAR-Si Goal	MG-Si Actual
Al	100	4300
B	0.8	36
Ca	600	590
Cr	700	310
Cu	900	90
Fe	800	8000
Mn	300	200
Mo	1400	<10
Ni	800	80
P	1.6	44
Ti	50	410
V	40	160
Zr	1300	30

C. Silica

1. General Survey

River-bed gravel is commonly used as the source of quartzite in the commercial production of MG-Si. Although this quartzite has not been extensively analyzed under this contract, it is clear that its aluminum concentration is the major deterrent in its use as a raw material for SoG-Si production. Aluminum contents have been analyzed to be in the 300-500 ppmw range as compared to the goal of 60 ppmw.

The existence of deposits in North America of sand, quartzite, and quartz, having sufficient purity for the hydrothermal growth of quartz for piezoelectric applications, has been reported by Kolb, et al. (8).

Dow Corning and Interlake, Inc. performed a survey of over 90 foreign and domestic sources of silica to ascertain their location and accessibility, representative composition, and estimated commercial price. State geologists were contacted, where possible, to verify reported information. Samples for analysis were received from 36 domestic and foreign sources. Boron and phosphorus were always determined due to the low concentrations required. Aluminum and iron were analyzed occasionally since they are the only other impurities detectable in high-quality silica. Experience early in the program indicated that other impurities were not present above the usual 5 to 10-ppmw detection limit of the analytical technique.

Results of the complete survey have been reported (7). A selection from the report of the most promising high-purity silica sources is given in Table 4. Domestically it appears that the best source of quartz is from Arkansas where a large number of veins break the surface from a general belt of quartz that is 130 km wide by 300 km long. Two suppliers were identified who estimated their prices for quartz to range from \$0.11-0.24/kg in tonnage quantities.

Table 4. Some Foreign and Domestic Sources of High-Purity Silica.

Company and Address	Impurity (ppmw)				Comments
	Al	B	Fe	P	
<u>Canada</u>					
<u>British Columbia</u>					
Mount Rose Mining Co., Ltd. North Vancouver V7J2J6	30	<1	3	5	80,000 MT proven quartz reserve; \$0.66/kg
<u>Ontario</u>					
Comet Quartz, Ltd. Whitby L1N5S	-	2	5	2	1x10 ⁸ MT quartz reserves; \$0.20/kg
<u>United States</u>					
<u>Arizona</u>					
Hemphill Bros., Inc. Kingman 86402	-	2	8	3	Quartz
<u>Arkansas</u>					
Malvern Minerals Co. Hot Springs 71901	20	<1	20	<5	\$0.15-0.24/kg; quartz (see text)
Quartz Processing Corp. Hot Springs 71901	-	<1	<5	<5	\$0.11/kg; quartz (see text)
<u>Massachusetts</u>					
Sobin Chemical Boston	170	<1	50	<5	Quintus quartz sand; \$0.22/kg
<u>Montana</u>					
Holand, Donald Fargo, ND 58102	-	1	66	<5	New quartzite deposit being developed.

Quartz prices and transportation charges limit the selection of foreign silica sources to Canada. Dow Corning chose to work with Mount Rose Mining Company which has 80,000 MT of proven reserves in British Columbia. This material currently sells for \$0.66/kg in small tonnage quantities. Sources similar to the Mount Rose deposit have been identified in British Columbia.

2. Compositional Analysis of Quartz

Detailed compositional analyses have been made of 4.5 Mg of quartz supplied by Malvern Minerals Company of Arkansas and of 13 MT of quartz purchased from Mount Rose Mining Company of British Columbia. Individual analyses of 65 samples appear in Appendix A. The average analyses taken from appendix A are summarized in Table 5. Averages calculated from actual measurements and "less-than" numbers assumed the latter to be equal to zero; i.e., the average of the two measurements 50 and <10 is $(50+0)/2 = 25$. This averaging method distorts the Fe and P averages in Appendix A4 since low determinations were averaged with "zero" values.

Table 5. Average Analyses of Various Quartz Samples Abstracted from Appendix A.

Average Impurity (ppmw)	Arkansas			British Columbia Milky	Goal
	Clear	Semi-Clear	Milky		
Al	20	40	20	20	60
B	<1	3	1	2*	1
Fe	<10	20	20	5	500
P	<10	<10	<5	2	5

*One group of 5 samples averaged 5 ppmw; the remaining 13 samples average <1 ppmw.

Since the analyses reported in Table 5 are very close to the detection limit for each impurity, the quartzes must be considered to be indistinguishable. The estimated error in the analysis near the detection limit is at least $\pm 100\%$ and probably higher. A more sensitive technique is required to distinguish differences between various quartzes.

The boron analyses in Table 5 must be further qualified by results obtained from analyses of quartz from a U.S. Fused Quartz Czochralski crucible and of Dow Corning semiconductor-grade silicon. The boron concentration in the crucible quartz was analyzed to be 8 ppmw as compared to a specification of < 0.6 ppmw. In the semiconductor silicon, the boron level was reported to be 6 ppmw by emission spectroscopy as compared to a specification of < 0.0001 ppmw as determined by electrical resistivity. These data point out the difficulties encountered in measuring impurity levels in the sub-ppm to ppm level in silicon and quartz.

In summary then, it appears that quartz samples are available that meet the purity requirements of this program. Absolute verification of this can only be accomplished through measurement of the silicon produced using electrical resistivity measurements.

3. Decrepitation of Quartzes and Quartzites

Silica samples must be able to withstand the high thermal and mechanical stresses that they are subjected to in the direct arc reactor. If they do not, they decrepitate into small particles that become entrained in the off-gases resulting in lower silicon yields.

Decrepitation testing of a variety of quartz samples was performed in order to develop experience in using this method to characterize the samples with respect to their probability of being able to be successfully used in a commercial-size direct arc reactor. The testing was carried out in a manner similar to the technique used for many years at Elkem-Spigerverket's R&D Center in Kristiansand, Norway. The test method is able to sort out quartz samples that are unsuitable for smelting; however, it does not guarantee that the promising samples will smelt well.

The decrepitation test involves determining the mechanical strength of the quartz after it is thermally stressed at high temperature. To carry out a decrepitation test, a quartz sample is crushed into the size range of 20-25 mm. The samples are placed in a graphite crucible and introduced into a tube furnace maintained at 1300 °C. Samples are held in the tube for approximately one hour and are then withdrawn from the furnace and cooled to room temperature. The percentage quartz retained on a 2-cm screen after screening gives an indication of the thermal shock resistance of the sample. To find the mechanical strength of the quartz, the sample is placed in a cylindrical container equipped with a lid. The container is inverted upside-down 100 times. The amount of quartz retained on a 0.5-cm screen after screening determines the mechanical strength of the quartz.

The decrepitation tests of various samples of quartz obtained from different sources are summarized in Table 6. Material is considered to be of suitable mechanical strength for arc-furnace smelting if 60 % of it remains on the 0.5-cm screen. Of the sixteen samples tested, all samples named 'Eureka' are considered to be of unsuitable quality for smelting. These quartzite samples do not have their quartz particles strongly enough "glued" together.

Testing of the selected Arkansas and British Columbia quartz samples in the 200-kVA direct arc reactor showed their actual physical strength to be in agreement with the measured decrepitation characteristics. No DAR experiments were made to verify the negative decrepitation data concerning quartzites.

4. Quartz Sand

Sand, i.e., unbound particles of quartz, is a potential source of silica in the direct arc reactor. Compositional analysis, such as that for Quintus quartz (\$195/MT) in

Table 6. Decrepitation Characteristic of Various Quartz Samples

Source	Retention on 0.5-cm Screen (%)
ANGOLA	
Thermal American Fused Quartz Co. Montville, NJ 07045	68
AUSTRALIA	
General Superintendence Co. Sydney	93
CANADA	
Mount Rose Mining Co., Ltd. North Vancouver, BC V7J2J6	92
Independent Design and Review Mount Laurel, NJ 08054	70
UNITED STATES	
Arkansas	
Malvern Minerals Co. Hot Springs	
Milky, Garland Co.	77
Milky, Saline Co.	82
Semiclear	63
California	
Nopak Range	
Eureka 8815*	48
Resting Spring Range	
Zabriskie 8814*	82
Nevada	
Arrow Canyon Range	
Eureka 8818*	30
Bare Mountain	
Eureka 8813*	12
Eureka 8814*	94
Pahranagat Range	
Eureka 8817*	35
North Carolina	
Material Sales Co. Lilesville 28091	78
South Dakota	
Pacer Corp. Custer 60018	84
Utah	
Crystal Peak Eureka 8819*	13

* Obtained from K. Ketner, Geological Survey, Dept. of Interior, Denver Colorado.

Table 4, indicates that sand can be of the same quality as massive quartz. Sand in fact can be purified by chemical treatment due to its much higher surface area as compared to massive quartz. Sand should also be of more uniform and consistent chemical composition since it has been classified over eons.

Sand must be pelletized to roughly 2-cm diameter pellets before it can be used in a direct arc reactor. Sand could be possibly pelletized as sand pellets or in conjunction with a powdered carbon reductant such as carbon black or activated carbon.

Sand has not been tested as a silica source in the Dow Corning Process. It has attributes, however, that makes it interesting for further investigation.

D. Carbon

1. Reductants

a. General

The need in this program to use a carbon reductant for silica that is purer than the commercial reductants for the production of MG-Si is obvious from Table 7. The maximum permissible levels of impurities in carbon are exceeded in several cases for all three reductants.

Purification of carbon was seriously considered due to the success of reducing boron to less than 1 ppmw in graphite used for the nuclear industry. Charcoal purification was concentrated on while purification of lignite and petroleum coke was investigated to a lesser degree. The use of sugar char as a reductant was also considered. The results of all these studies will be described in a later section. The next section delineates the results obtained with the most favorable carbon reductants: activated carbon and carbon black.

b. Activated Carbon and Carbon Black

i. As-Received Material

A successful reductant for the carbothermic reduction of silica in the DAR must meet the two primary prerequisites of purity and chemical reactivity: these do not necessarily go hand-in-hand.

The purity was determined of various samples of carbon black and activated carbon. Table 8 summarizes analyses of activated carbons that meet, or nearly meet, purity requirements. Those samples for which impurities exceed their established maxima are listed in Appendix B. The activated carbons, which were supplied in the form of pellets, are quite pure with respect to the goal. Limited analyses of samples prepared by concentrating solutions of dissolved material showed that the goals (see Table 8) for boron and phosphorus can also be reached. A later section will show that activated carbons meet the second prerequisite of adequate chemical reactivity in the DAR.

TABLE 7. ANALYSES OF CARBON REDUCTANTS USED TO COMMERCIALY PRODUCE MG-Si.

Impurity (ppmw)	Coal	Petroleum Coke	Wood Chips	Calc. Max. in Carbon for SoG-Si*
Al	4600	220	290	100
B	26	<1	14	1
Ca	340	90	4300	1000
Fe	1800	500	410	1000
Ti	440	80	23	70
V	10	540	<10	50

* See Table 2.

TABLE 8. AVERAGE ANALYSES OF ACTIVATED CARBON SAMPLES THAT MEET PURITY GOALS.

Impurity (ppmw)	Carbon Goal	Sample Number				
		AC3	AC9	AC10	AC11	AC12
Al	100	80	80	30	10	10
B	1	<5	<5	<5*	<5	<5
Ca	1000	10	60	10	10	30
Cr	1000	<10	10	<10	<10	<10
Cu	1000	<5	30	<5	<5	5
Fe	1000	10	590	100	470	520
Mn	600	<10	<10	<10	<10	<10
Mo	2000	<10	<10	<10	<10	<10
Ni	1000	<10	<10	20	<10	<10
P	10	<10	20	<10*	<10	<10
Ti	70	<10	<10	<10	<10	<10
V	50	<10	<10	<10	<10	<10
Zr	1500	<10	<10	<10	<10	<10

* Concentration technique yields B<1, P=2 ppmw.

AC3: ICI Americas, Darco DXL-0-6838

AC9: Union Carbide, Columbia 3LXC 4/6

AC10: Acid washed AC9

AC11: Witco Chemical Corp., AC-5809

AC12: Witco Chemical Corp.

A high percentage of carbon blacks meets the carbon purity goals as indicated by the data in Table 9 for all 22 samples analyzed during the course of this work. Details concerning the suppliers of the samples are provided in Appendix C. All samples are produced from petroleum sources except for CB5 which is generated by the cracking of methane gas. Since this carbon black is one of the purer carbon sources, it was analyzed using a chemical concentration technique which showed <1 ppmw boron and 5 ppmw phosphorus.

ii. Pellets

All activated carbon and carbon black reductants were used in the form of pellets. Activated carbon from Union Carbide was supplied as ca. 3-mm-size pellets that were used either directly in the DAR or as a mixture with sucrose sugar cubes. The use of sugar cubes was found to increase the chemical reactivity of the dense activated carbon since the sucrose is converted to a high-surface-area sugar charcoal upon burning at the top of reactant mix in the DAR.

All carbon black reductants had to be pelletized to increase their micron-size particles to 5 to 25-mm-size pellets that would not be blown out of the DAR by the off-gases. Early experiments utilized binders such as starch, colloidal silica, silica flour, and their mixtures. Starches were not pure enough, especially with respect to phosphorus. Later experiments used carbon black bound with sucrose which is higher in purity. As in the case of activated carbon, sucrose was also found to increase the reactivity of the reactant mixture. Analyses of binders are shown in Table 10.

Carbon black pellets were normally prepared for Dow Corning by Mars Minerals, Inc. using special handling techniques. Drum pelletizers were used to produce all pellets except when sucrose was used as a binder. In this case, it was necessary to use a disc pelletizer. The analyses of the pellets are provided in Table 11. The purest pellets were prepared using carbon black from a CH₄ source with sucrose as the binder (see DAR-200-17).

TABLE 9. AVERAGE ANALYSES OF CARBON BLACK SAMPLES

Impurity (ppmw) *	Carbon Goal	Sample Number**										
		CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	CB9	CB10	CB11
Al	100	140	70	140	210	30	30	130	30	200	30	40
B	1	<5	<5	<5	<5	<5+	<5	<5	5	<5	<5	<5
Ca	1000	380	510	350	250	10	90	300	220	400	80	270
Fe	1000	80	40	25	40	20	10	40	20	80	60	50
P	10	<10	10	<10	10	10+	<10	<10	10	<10	<10	<10

Impurity (ppmw) *	Carbon Goal	Sample Number										
		CB12	CB13	CB14	CB15	CB16	CB17	CB18	CB19	CB20	CB21	CB22
Al	100	60	40	30	10	10	10	70	30	40	30	50
B	1	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Ca	1000	140	<110	110	80	460	<10	650	350	310	140	20
Fe	1000	30	60	40	30	40	20	100	50	10	10	60
P	10	10	50	<10	20	20	10	10	60	<10	<10	<10

* Cr, Mn, Mo, Ni, Ti, V, Zr <10 ppmw, each; Cu <5 ppmw.

** See cross reference of sample numbers and suppliers in Appendix C.

+ Analysis of pellets with 25% sucrose binder shows B<1 and P=5 ppmw using concentration techniques.

TABLE 10. AVERAGE ANALYSES OF BINDERS TO PRODUCE PELLETS

Impurity (ppmw)	Binders					
	Sucrose	Dextrin	OK Stabil.	Molasses	Ludox*	Silica Flour
Al	<10	210	210	130	240	300
B	<5	<10	<10	<5	<10	2
Ca	<10	120	180	910	20	130
Cr	<10	<10	<10	<10	<10	<10
Cu	<5	<10	<10	30	<10	<5
Fe	<10	<10	<10	140	70	180
Mn	<10	<10	<10	10	<10	<10
Mo	<10	<10	<10	<10	<10	<10
Ni	<10	<10	<10	<10	<10	<10
P	<10	180	40	500	90	30
Ti	<10	<10	<10	20	20	80
V	<10	<10	<10	<10	40	<10
Zr	<10	<10	<10	<10	10	110

* DuPont colloidal silica

TABLE 11. AVERAGE ANALYSES OF CARBON BLACK AND ACTIVATED CARBON PELLETS USED IN DAR EXPERIMENTS

DAR EXPERIMENTS												
IMP- URITY (ppmw)	DAR- 200-8	DAR-200-9		DAR- 200-10	DAR-200-11		DAR- 200-12	DAR- 200-13	DAR- 200-14	DAR- 200-15	DAR- 200-16	DAR- 200-17
		D+L*	D		S*	S+L						
Al	150	60	110	120	180	200	300	190	190	110	150	<10
B	6	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Ca	170	160	140	80	100	50	260	560	450	20	200	<10
Cr	10	<10	<10	<10	<10	<10	<10	<10	<10		<10	<10
Cu	5	50	<5	15	<5	9	<5	<5	8		6	<5
Fe	70	130	80	680	300	540	200	190	220	120	110	<10
Mn	<10	<10	<10	10	<10	20	<10	<10	<10		<10	<10
Mo	<10	<10	<10	<10	<10	<10	<10	<10	<10		<10	40
Ni	<10	<10	<10	<10	<10	<10	<10	30	<10		<10	<10
P	30	30	20	<10	50	50	<10	10	10	30	<10	<10
Ti	<10	<10	<10	<10	20	20	20	20	30	<10	10	<10
V	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zr	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

8: 81.2% CB9, 10.0% SiO₂ from Ludox, 8.8% OK Stabilizer

9: 80% CB9, 10% SiO₂ from Ludox, 10% dextrin; 90% CB9, 10% dextrin

10: 100% AC9

11: 75% AC3, 25% sucrose; 65% AC3, 25% sucrose, 10% SiO₂ from Ludox

12: 90% CB9, 10% OK Stabilizer

13: 80% CB9, 10% OK Stabilizer, 10% SiO₂ from Ludox

14: 80% CB9, 10% OK Stabilizer, 10% SiO₂ powder

15: 61% AC10, 39% sucrose as sugar cubes

16: 70% CB9, 30% sucrose

17: 75% CB5, 25% sucrose

* D = Dextrin, L = Ludox, S = Silica

c. Other Reductants

i. Charcoal

Wood charcoal contains too high concentrations of boron and phosphorus to be of use as a reductant to produce SoG-Si (9). Charcoal has been purified with freon at high temperatures to reduce the concentration of impurities (7,9,10) as seen in Table 12. Satisfactory reduction of the level of boron and phosphorus was found only at 2500 °C. However, this material was found to be nearly totally unreactive with quartz under normal operating conditions, as opposed to unpurified charcoal which is a fairly good reductant.

The purified charcoal was characterized by x-ray diffraction and chemical reactivity tests (7). X-ray diffraction patterns showed a broad and somewhat irregular peak in the vicinity of the graphite peak. The irregular peak increased in intensity with the temperature of charcoal purification and was not observed in the case of unpurified charcoal. Since change in chemical composition due to purification is minimal, significant structural change was indicated. This was particularly apparent from the noted volume decrease with purification temperature. Reactivity tests, according to a method reported by Tuset and Raaness (11), showed that purified charcoal had a somewhat lower ability to react with SiO(g) than did unpurified charcoal according to the reaction $\text{SiO(g)} + 2\text{C(s)} = \text{SiC(s)} + \text{CO(g)}$. However, it was still found to be more reactive than most reductants used for silicon production. It was therefore inferred that the formation of silicon carbide was not the rate-controlling reaction, but that its further reaction via $\text{SiC(s)} + \text{SiO(g)} = 2\text{Si(l)} + \text{CO(g)}$ was most likely the rate-controlling step. The reason for this may be that SiC is completely surrounded by silicon which blocks the contact between SiC and SiO. If so, the wetting property of SiC is important. In successful tests with unpurified charcoal, the silicon carbide was not surrounded by metal, but open for exposure to SiO (12).

TABLE 12. CHARCOAL PURIFICATION BY FLUOROCARBON TREATMENT

Impurity* (ppmw)	None	Purification Temperature (°C)			
		1500	1700	2000	2500
B	21	27	8	15	5
Ca	8800	30	90	30	30
Mg	200	<5	<5	<5	<5
Mn	120	<10	<10	<10	<10
P	230	25	160	20	<10
* Al, Cr, Cu, Fe, Ni, Ti, V, Zr. <10 ppmw					

Charcoal was dropped as a potential high-purity reductant due to its extreme unreactivity which results from its purification at high temperature.

ii. Lignite

Lignite has been used as a reductant for the production of metallurgical-grade silicon. However, lignite is too impure for the production of SoG-Si due to its high ash content - as shown in Table 8 - of nearly 20%.

Lignite briquets were subjected to chlorine purification at 2000 °C. Although the briquets did not lose their strength, the concentration of boron could not be reduced to low ppm-level required. X-ray intensity showed a continual increase with increasing severity of purification. Since x-ray intensity showed an indirect correlation with reactivity in the case of charcoal, increased purification temperatures were not attempted.

Lignite is considered to be a poor candidate as a reductant for the production of SoG-Si (13). It is anticipated to have many of the same problems as experienced in the past with charcoal. Since it is initially much more impure than charcoal, lignite was eliminated as a potential reductant.

iii. Petroleum Coke

This carbon material is one of the constituents used in the reductant mixture for the manufacture of MG-Si in the United States. A larger amount of petroleum coke is used in the mixture when MG-Si of higher purity is required. However, a trade-off exists since petroleum coke is the least reactive component of the mixture. An effort was made to enhance the reactivity through expanding its structure by intercalation (13). Although this resulted in a doubling in the surface area of the coke, the surface area was still too low to effectively change its reactivity. Since acid washing did not enhance the purity of the coke either, this reductant was eliminated from the program.

iv. Sugar Charcoal

Dr. Robert Rhein of JPL suggested sugar char as a potential carbon reductant based upon its purity - see Table 6 and upon the copious amount of information he found in the literature concerning its pyrolysis and conversion to charcoal.

The cost of sugar, itself, on an equivalent weight of silicon basis, was determined from its cost of \$0.061/lb* when purchased in 112,000-lb quantities. The equivalent cost is determined below based on an overall process yield for silicon of 72%. Also included is the fixed carbon value of 15.0 % (85.0 % volatiles, 0.0 % ash).

$$\frac{\$0.061}{\text{lb}} \cdot \frac{2.2 \text{ lb}}{\text{kg sugar}} \cdot \frac{1 \text{ kg sugar}}{0.15 \text{ kg carbon}} \cdot \frac{24 \text{ kg carbon}}{28 \text{ kg silicon}} \cdot \frac{1}{0.8} \cdot \frac{1}{0.9} = \frac{\$1.07}{\text{kg Si}}$$

The cost of slightly over \$1/kg Si does not include the cost of converting sugar to sugar charcoal. Therefore, sugar char is too expensive for the goals of this program.

Several avenues of approach for sugar exist; however:

- use of sugar directly in the DAR where charring occurs *in situ*.
- use as an additive to the main carbon reductant so as to cause increased bed porosity due to sugar swelling during charring.
- use as a binder for the main reductant.

2. Electrode

Graphite electrodes are used to supply the arc for obtaining high temperature for the carbothermic reduction process within the DAR. Experience in our equipment has shown that the consumable graphite electrode contributes in the neighborhood of 7 % of the carbon utilized during silicon production. Therefore, it has been necessary to purify graphite electrodes to minimize contamination. Ultracarbon Corporation has supplied 8 to 15-cm-diameter electrodes that were purified at 2500 °C under a fluoro-carbon atmosphere (10). A recent analysis of an electrode used in experiment DAR-200-18 appears below.

* Wall Street Journal, July 21, 1978.

TABLE 13. ANALYSIS OF A PURIFIED 15-CM-DIAMETER ELECTRODE

Impurity	Concentration (ppmw)
Al	<10
B	<1
Ca	<10
Cr	<10
Cu	<5
Fe	<10
Mn	<10
Mo	<10
Ni	<10
P	5
Ti	<10
V	<10
Zr	<10

V. SILICON PRODUCTION, STEP

A. Summary

Reactors of 50-kVA and 200-kVA size were used to study the production of silicon using three different reductants for quartz: charcoal, activated carbon, and carbon black. Charcoal was eliminated as a possible reductant because it becomes very unreactive when purified at high temperature. Carbon black/sucrose mixtures are superior to activated carbon with respect to reactivity, energy consumption, and purity.

The best experiment utilizing carbon black/sucrose pellets gave 128 kg Si during a 50-h experiment corresponding to an effective silicon production rate of 2.9 kg/h. Energy usage was favorable in a small experimental reactor at only 26 kWh/kg Si. Typical silicon produced from such experiments contained 50-100 ppmw of aluminum and iron and less than 10 ppmw each of other impurities.

B. Experimental

1. General

Silicon was produced in two, somewhat similar direct arc reactors during the course of the contract. Early experiments were performed from September, 1976 to August, 1977 in a 50-kVA reactor (DAR-50) located at Elkem-Spigerverket's R&D Center in Kristiansand, Norway. Later experiments were performed during the period from February to October, 1978 in a 200-kVA reactor (DAR-200) purchased by Dow Corning from Elkem-Spigerverket.

DAR-50 is shown in cross-sectional view in Figure 3. Dimensions are in millimeters. The DAR is divided into a separate upper and bottom section. The upper section is divided into two sections along its axis. A 50% Al_2O_3 / 50% SiO_2 ceramic lining is contained within a cast iron shell.

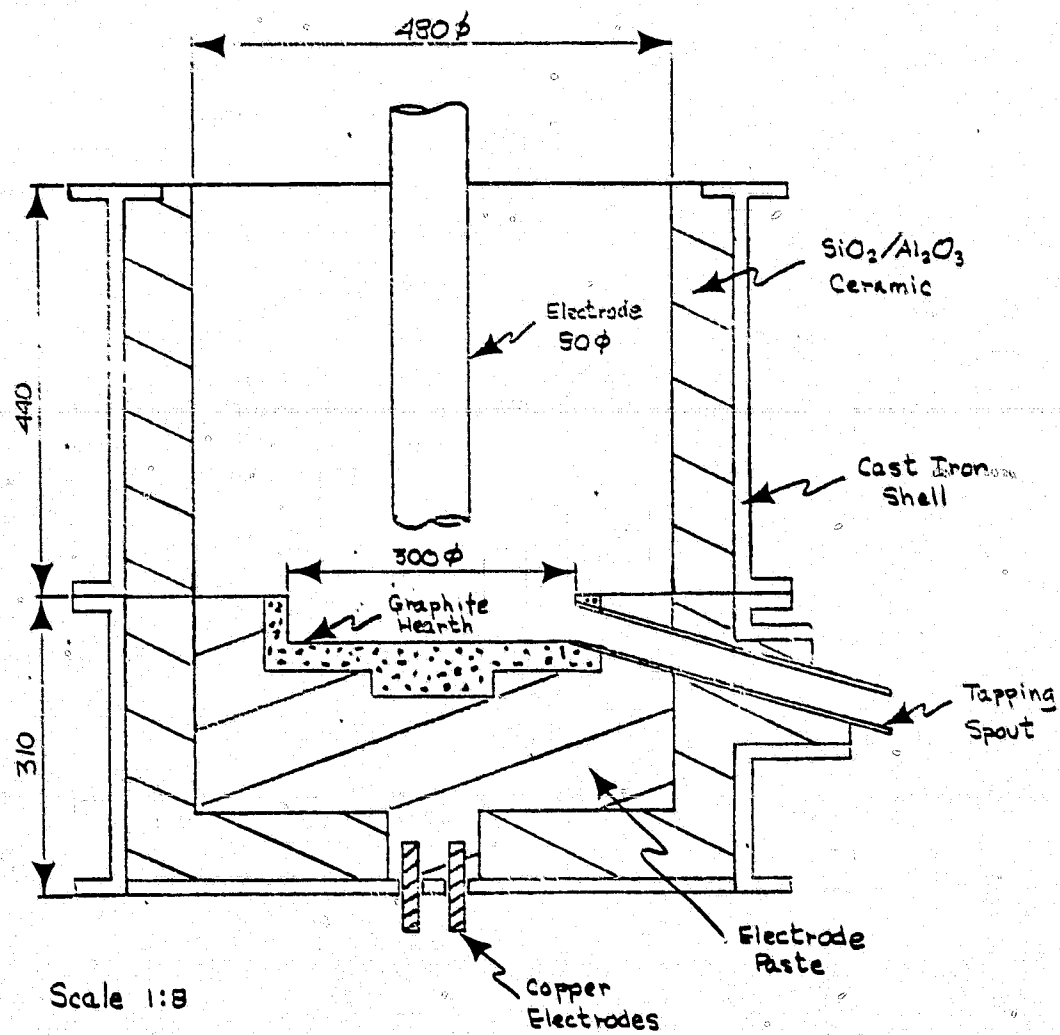


FIGURE 3. Dimensions and Construction of DAR-50

The bottom section of the DAR is ceramic lined and contains electrode paste which provides circuit completion for the arc struck between the electrode and the graphite hearth. The external power supply is connected to the graphite electrode at the top and to the copper electrodes inbedded in the carbonized paste at the bottom. A spout is provided for tapping silicon metal from the graphite hearth. The spout consists of graphite coated with chemically-vapor-deposited silicon carbide.

DAR-200 is a much-improved version of DAR-50. The main differences, however, are in the larger size smelting pot (60-cm I.D.) and electrode (15-cm I.D.). Changes in the electrical system provided for much more control of the carbothermic reduction process.

The ceramic liner used in the DAR has potential of contributing significant impurities to the smelting process. This potential was minimized through pre-contract experiments that pointed out values for reactor parameters which provide insulation of the ceramic liner by unreacted raw materials from the high-temperature smelting zone. This is easily done by maintaining the electrode diameter small enough so as to not form too large of a cavity within the reactor (see Fig. 4). Such an insulation effect can also be attained by employing a sufficiently large reactor diameter once an optimum electrode diameter has been determined. Figure 4 shows the cross section of the DAR after half of the upper hearth section was removed following a successful experiment. The cavity that surrounds the electrode had its walls formed by strong sintered material consisting of partially reacted raw materials and silicon carbide. Unreacted raw materials are shown external to the cavity walls.

Experiments were run somewhat similarly. Quartz was crushed and screened to $-30 + 5$ mm size while the carbon size varied considerably. These materials were charged to the DAR every 1-2 h in a mixture having greater than 100%

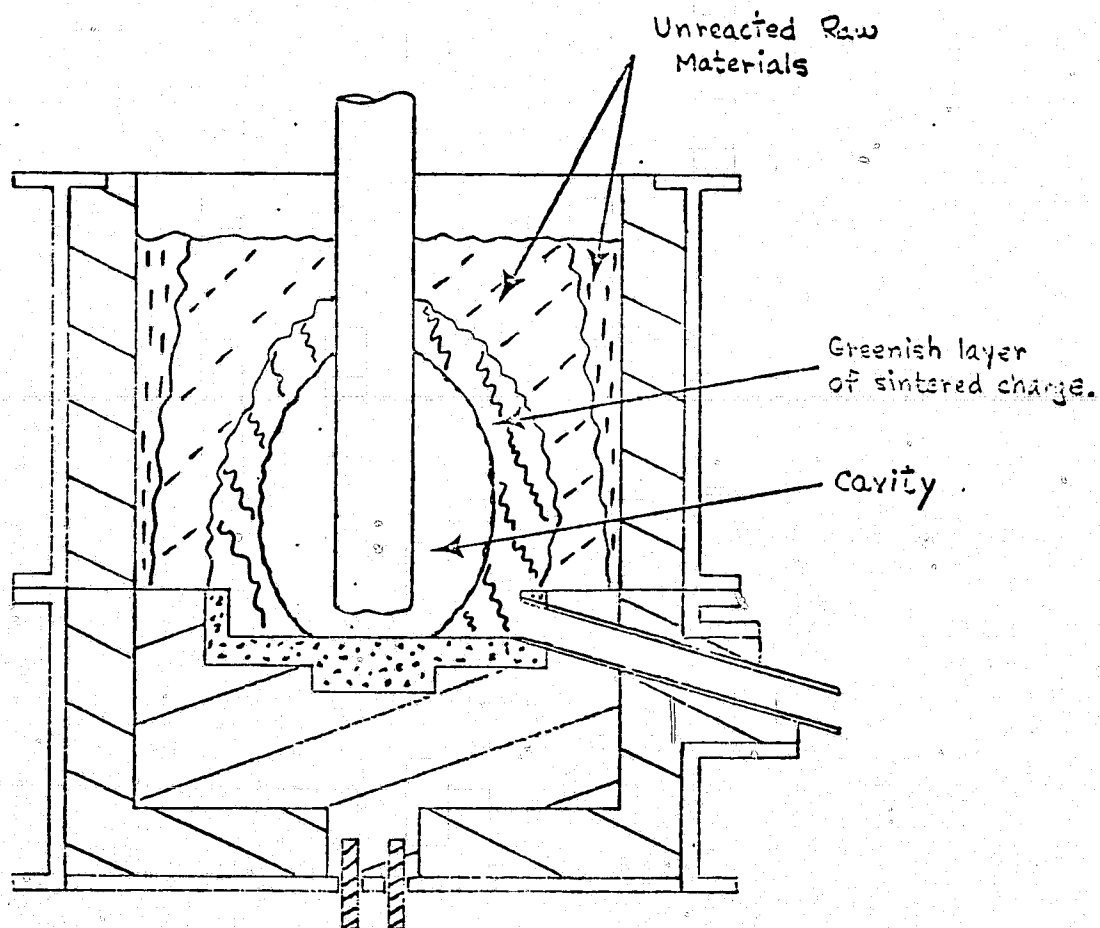


FIGURE 4. Cross-Sectional View of the DAR after Successful Silicon Smelting

ORIGINAL PAGE IS
OF POOR QUALITY

carbon content*. Such an amount of carbon causes the formation of silicon carbide, which is required for later silicon production, at the bottom of the furnace. After 8-24 hours, the carbon content was reduced to provide suitable reaction conditions for producing silicon.

At the end of a 1 to 2-h period, silicon was removed from the DAR. The walls of the cavity around the electrode were then crushed with graphite rods. A new charge of raw materials was added to the furnace and smelting was continued for another 1 to 2-h period.

DAR-50 was run at 40 kW with the voltage between the hearth and the electrode varying from 30-40 V. Reaction conditions were controlled by varying the distance between the tip of the electrode and the hearth. DAR-200 was operated at about 80 kW with the potential varying from about 50-60 V.

2. Charcoal as Reductant

Experiments centering around purified charcoal as a reductant represented 18 of the total 28 experiments carried out under this contract. The first eleven experiments were performed at Elkem in DAR-50 in order that Dow Corning personnel could obtain the needed technology for further investigations at Dow Corning. In addition, DAR-50 is the only small-scale, easily accessible reactor known to be available for work of this type. The remaining seven charcoal experiments were carried out at Dow Corning in DAR-200.

Data for the various charcoal-reductant experiments are presented in Table 14. Tests were made with commercial reductants* to establish baseline operating conditions. Runs were also made with unpurified charcoal to determine baseline parameters from which to compare experiments utilizing purified charcoal.

* 100% carbon content represents the stoichiometric amount of carbon, i.e., two g-atoms of carbon per mole of SiO_2 .

* Coal, coke, and wood chips.

TABLE 14. DATA FOR SILICON PRODUCTION USING CHARCOAL AS A REDUCTANT

Run No.	Quartz	Carbon	Aver. Carbon Content (%)	Total Time (h)	Electrode Consump. (g/h) *	Wt. Si Produced (kg)	Aver. Rate (kg/h)	Aver. Energy (kWh/kg)
DAR-50-1	Norwegian	Charcoal	-	45	-	30	0.7	48
2	Arkansas	Charcoal	-	26	-	12	0.5	55
3	Arkansas	Commercial	-	26	-	14	0.5	44
4	Arkansas	Char. (2500°)	-	15	0	0.3	0	-
5	Arkansas	Char. (2000°)	-	30	970	4	0.1	188
6	Arkansas	Charcoal	-	30	200	15	0.5	60
7	Arkansas	Char./Char. (2000°)	-	27	220	12	0.4	56
8	Arkansas	Char. (1700°)	91	26	360	0.7	0	-
9	Brit. Colum.	Char. (1700°)	93	22	150	4	0.2	128
10	Brit. Colum.	Char. (2000°)	92	17	160	0.2	0	-
11	Brit. Colum.	Char. (1900°)	95	29	160	8	0.3	64
DAR-200-1	Arkansas	Commercial	-	36	660	42	-	-
2	Arkansas	Charcoal	110	30	594	43	1.8	34
3	Arkansas	Charcoal	99	48	361	110	2.6	29
4	Brit. Colum.	Charcoal	98	34	141	52	1.5	37
5	Brit. Colum.	Charcoal	98	35	435	62	2.0	38
6	Arkansas	Char. (coconut)	-	14	328	4	-	-
7	Arkansas	Char. (2200°)	-	36	468	44	2.2	36

The important message to be gained from the data in Table 14 is that it is difficult to produce large quantities of silicon using purified charcoal as a reductant. Consequently, low production rates occur with accompanying high energy usage. These trends are more obvious when it is realized that extraordinary operating conditions had to be used to make the silicon that was obtained. It is believed that such conditions, e.g., a low carbon content in the 80-8 range, cannot be used to commercially produce silicon. The problem of poor charcoal reactivity is treated in depth in the earlier "Raw Materials" section of this report.

Emission spectrographic analyses of the silicon produced from charcoal-reductant experiments are provided in Tables 15 and 16. Samples were obtained by melting down 1 kg of DAR-Si in a Czochralski puller to homogenize the sample. A sample of silicon was withdrawn by suction casting it in a small diameter quartz tube to quickly solidify it, thereby minimizing segregation of impurities. This sample, after removal from the tube, was submitted for analysis. The use of purer raw materials obviously resulted in production of purer silicon. The data also confirms, in specific instances, that the gain in purity through use of better raw materials can be offset by use of inconsistent purification of charcoal, contamination of the raw materials by further handling after purification, and by contamination of the reactants in the reactor by airborne materials or by accidentally dropping contaminants into the reactor.

Boron and phosphorus analyses were performed on DAR-Si that had gone through the purification step. These analyses are provided later.

3. Carbon Black and Activated Carbon as Reductants

Attention was focused on carbon black and activated carbon as reductants due to their low levels of impurities as indicated by emission spectrographic analysis. Three silicon production experiments were performed using activated carbon while six tests were made with carbon black

TABLE 15. ANALYSES OF SILICON PRODUCED USING CHARCOAL AS A REDUCTANT IN DAR-50

Impurity	Concentration of Impurities for Various DAR Experiments (ppmw)								
	MG-Si	-1	-2	-4	-5	-6	-7	-9	-11
Al	3400	300	40	110	420	40	110	50	190
Ca	480	6500	1400	80	50	260	210	620	230
Cr	290	<10	<10	<10	<10	<10	<10	10	<10
Cu	70	30	20	<5	10	10	<5	5	10
Fe	7100	3900	4000	220	290	190	120	250	490
Mg	<5	70	20	<5	<5	10	<5	20	<5
Mn	180	340	320	<10	<10	60	<10	20	<10
Ni	80	90	20	<10	<10	<10	<10	20	<10
Ti	330	90	10	<10	20	60	20	40	30
V	170	30	20	<10	<10	<10	<10	<10	<10
Zr	20	-	-	<10	<10	<10	<10	<10	<10

TABLE 16. ANALYSES OF SILICON PRODUCED USING CHARCOAL
AS A REDUCTANT IN DAR-200

Impurity	Concentrations of Impurities for Various Experiments (ppmw)						
	MG-Si	-2	-3	-4	-5	-6	-7
Al	3400	160	100	40	140	2800	1800
Ca	480	7900	850	2900	2000	200	550
Cr	290	<10	10	<10	<10	30	<10
Cu	70	20	10	15	20	45	40
Fe	7100	15000	3600	1100	2100	3200	11000
Mn	180	340	180	420	650	40	60
Mo	-	<10	<10	<10	<10	<10	<10
Ni	80	380	20	<10	<10	<10	<10
Ti	330	40	110	30	50	250	370
V	170	<10	<10	<10	<10	30	20
Zr	20	<10	<10	<10	<10	<10	40

pellets bound with either various starches or sucrose. While data from these experiments are somewhat limited in quantity, the conclusions drawn from the data base are confirmed by later experiments performed after contract termination.

Data from experiments DAR-200-8 to 17 are provided in Table 17; further raw material data appear in the "Raw Material" section. Ignoring test DAR-200-12, due to a broken electrode, 100-% carbon content appeared to be about correct for both reductants. Runs of 23-60 h resulted in 28 to 128-kg quantities of silicon (1.3-2.9 kg/h beginning with initial silicon production). Energy consumption varied from 26-47 kWh/kg.

Conclusions concerning experiments with carbon black and activated carbon reductants are more easily drawn from averaged data shown in Table 18. To preface such conclusions, however, it must be stated that no measurable difference in any reaction parameters could be detected as being due to the source of quartz. The effect of adding sucrose cubes (0.9 cm) to activated carbon pellets (0.5-cm diameter), so that the sucrose represented from 20 to 35% of the total fixed carbon, had no effect on either silicon production rate or energy usage within experimental uncertainty.

The use of carbon black/sucrose pellets (0.6 to 1.0-cm diameter) having 30% by weight sucrose resulted in substantially higher silicon production rates as compared to carbon black/starch pellets or any pellets containing activated carbon. Additionally, lower energy consumption (kWh/kg Si) also occurred when using carbon black/sucrose pellets.

It is clear at this point then, that carbon black pelletized with sucrose is the preferred reductant from the standpoint of reaction conditions in the DAR.

The purity of silicon produced using activated carbon and carbon black as reductants is shown in Table 19.

TABLE 17. DATA FOR SILICON PRODUCTION USING ACTIVATED CARBON AND CARBON BLACK REDUCTANTS

Exper. DAR- 200-	Quartz Source	Carbon Reductant	Aver. Carbon Content (%)	Total Time (h)	Electrode Consump. (g/h)	Wt. Si Produced (kg)	Aver. Rate (kg/h)	Aver. Energy (kWh/kg)
8	Arkansas	CB9/starch	83	31	350	28	1.5	36
9	Arkansas	CB9/starch	97	36	304	56	2.0	34
10	Arkansas	AC9	99	35	306	56	1.8	29
11	Arkansas	AC3	100	23	362	33	2.0	28
12	Brit. Colum.	CB9/starch	87	27	393	14	0.9	78
13	Brit. Colum.	CB9/starch	102	30	384	33	1.3	47
14	Brit. Colum.	CB9/starch	102	24	364	31	1.8	43
15	Brit. Colum.	AC10 & Sucrose	100	60	380	100	1.8	33
16	Brit. Colum.	CB9/sucrose	-	50	317	128	2.9	26
17	Brit. Colum.	CB5/sucrose	99	58	254	128	2.4	26

**TABLE 18. SUMMARY OF SILICON PRODUCTION EXPERIMENTS
DETAILED IN TABLE 17.**

Reductant	Time (h)	Silicon Wt. (kg)	Aver. Rate (kg/h)	Aver. Energy (kWh/kg)
AC	29	45	1.9	29
AC & Sucrose	60	100	1.8	33
CB/Starch	30	37	1.7	40
CB/Sucrose	54	128	2.7	26

TABLE 19. ANALYSIS OF SILICON PRODUCED USING ACTIVATED CARBON AND CARBON BLACK
AS REDUCTANTS IN DAR-200.

Impurity	max.*	Concentration of Impurities for Various DAR Experiments (ppmw)									
		-8	-9	-10	-11	-12	-13	-14	-15	-16	-17
Al	100	80	50	270	320	320	280	80	150	100	70
Ca	600	<10	40	<10	<10	80	300	40	60	40	50
Cr	700	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cu	900	60	<5	8	<15	<5	<5	<5	<5	<5	<5
Fe	800	1700	140	1100	14000	2700	470	50	460	50	80
Mn	300	20	<10	<10	150	<10	10	<10	<10	<10	<10
Mo	1400	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ni	800	<10	<10	10	50	50	<10	<10	<10	<10	<10
Ti	50	70	20	30	50	<10	40	20	30	<10	<10
V	40	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zr	1300	<10	<10	<10	<10	<10	10	<10	<10	<10	<10

* See "Raw Materials" Section.

Earlier experiments produced silicon of less purity, especially Fe and Al, since determining reactivity was of a higher priority than obtaining purity. Activated carbon presented a problem with respect to iron due to generally being present in the activated carbon samples themselves. Later experiments with carbon black, DAR-200-14, 15 and 16, represent what we believe can be produced on a consistent basis, i.e., Al and Fe of 50-100 ppmw, with all other impurities being less than 10 ppmw.

Calcium is not a problem since it vaporizes upon melting and holding silicon for a short time. Boron and phosphorus analyses were performed after Czochralski growth and are reported in the next section.

The impurity analyses of DAR-Si as indicated in the latter runs in Table 19 meet or exceed the specifications for SoG-Si that were outlined in Table 1.

VI. SILICON PURIFICATION STEP

A. Summary

Impurity segregation was shown to be the same for polycrystalline silicon growth as it is for single-crystal growth if a reasonably dilute melt is used in order to prevent constitutional supercooling. DAR-Si was purified by growing SoG-Si poly-ingots using the Czochralski technique. Compositional analysis of the poly-ingots showed them to meet all Dow Corning-set specifications for impurity concentrations, except for boron. However, the concentration of boron is near that reported by others to give maximum solar cell efficiency. The usable poly-ingot yield from DAR-Si was shown to be 77%. Suggestions to improve the yield were made. Growth of single-crystal silicon from the SoG-Si poly-ingots was demonstrated.

DAR-Si purification via Bridgman-type crystal growth was shown to be feasible as well as potentially more cost effective than Czochralski crystal growth. Since resources were not available to more fully develop this technique, it was abandoned in favor of the more technically sophisticated Czochralski method.

Attempts to purify silicon of metallurgical-grade purity using vacuum evaporation were totally unsuccessful.

B. Czochralski Crystal Growth

1. Impurity Segregation During Growth of Poly-Silicon

Czochralski crystal growth of an ingot from DAR-Si feed stock always resulted in polycrystalline material. This most likely is due to the 100-ppm concentrations of aluminum and iron in DAR-Si. Therefore, the effect of polycrystalline growth on effective segregation coefficient was investigated prior to the onset of constitutional supercooling of the melt.

Copper and manganese were used to dope semiconductor silicon since the concentrations of both impurities can be accurately determined by thermal neutron activation analysis. Ingots of 3.5-cm diameter were pulled at 11.5 cm/h in a NRC, Model 2805, crystal puller.

In one growth experiment a single-crystal seed was used and pulling continued until loss of crystalline structure, due to constitutional supercooling, was observed. A polycrystalline seed was used in the second experiment and polycrystalline ingot growth allowed to proceed until feathering of the outer ingot surface was observed indicating the onset of constitutional supercooling; (see the bottom of the large ingot indicated in Figure 5) Grain size was such as to produce a grain density of $20/\text{cm}^2$.

Samples were selected from the full-diameter region of the ingots just below the seed, from the region just above the point where constitutional supercooling occurred, and from the tang end of the ingots (approximately 4 cm after constitutional supercooling occurred). The samples were analyzed by neutron activation analysis for copper and manganese concentrations.

Results are shown in Table 20 for analyses of the single-crystal seed sample, polycrystalline seed sample, single and poly samples taken just prior to the onset of constitutional supercooling, and finally the respective tang-end samples. The concentrations and, therefore, the effective segregation coefficients for the various regions are, for all practical purposes, identical for single-crystal and polycrystalline material. Relatively larger

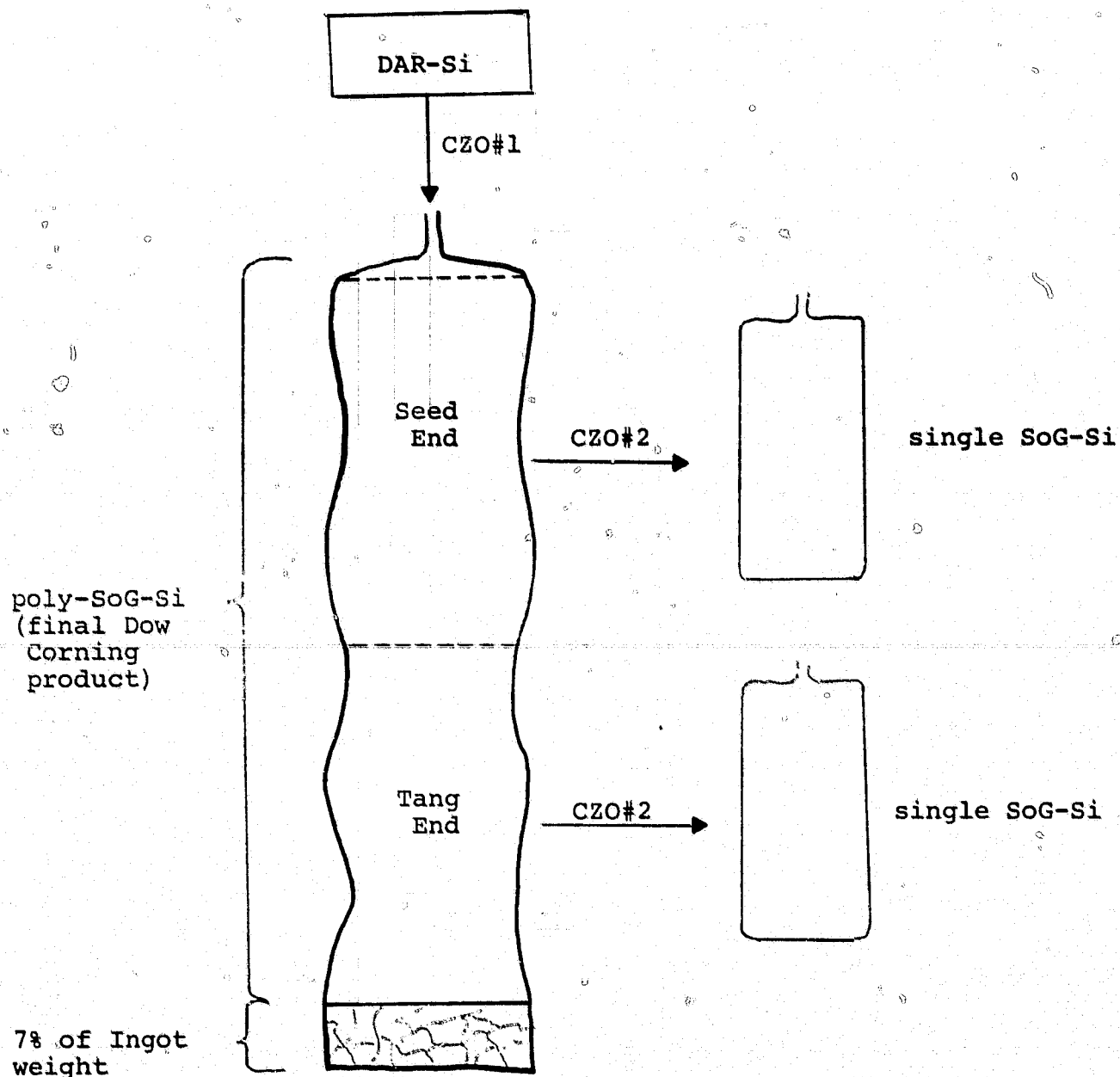


FIGURE 5. SCHEMATIC OF SILICON PROCESSING DURING CZOCHRALSKI CRYSTAL GROWTH STUDIES

TABLE 20. Comparison of Purification by Czochralski Freezing of Single-Crystal and Polycrystalline Silicon Ingots.

Sample Identification		Impurity Concentration (ppma)		Effective Segregation Coefficient	
Seed Type	Sample Position	Mn	Cu	Mn	Cu
Single Poly	Near seed	0.028	0.085	1.2×10^{-5}	4.25×10^{-4}
		0.026	0.077	1.13×10^{-5}	3.85×10^{-4}
Single Poly	Before loss of structure	133	3.34	5.7×10^{-2}	1.67×10^{-2}
		198	5.26	8.6×10^{-2}	2.6×10^{-2}
Single Poly	Near tang	988	32.9	0.429	0.16
		1090	29.2	0.473	0.14

differences exist at the points just prior to the onset of constitutional supercooling; however, rapid changes are occurring in this region and slight differences in the sample site could easily explain the observed variation. The relatively high concentration prior to the occurrence of constitutional supercooling has been observed in other ingots and is attributed to impurity trapping during cellular growth. Once constitutional supercooling occurs, the effective segregation coefficients increase from near their equilibrium values in the seed end of the ingots to very large values approaching 0.2 for copper and 0.5 for manganese.

These data imply that polycrystalline ingot growth is just as effective as single crystalline ingot growth for segregating impurities from the solid into the melt. The data also suggest that segregation is less efficient for melts more concentrated in impurities. However, the impurities in DAR-Si are low enough in concentration, as shown in Section VI.B.2.b, such that segregation is a very efficient purification technique for this material.

Higher growth yields of polycrystalline ingots are expected compared to the yields experienced for single-crystalline ingots in the semiconductor industry. This is because growth is terminated upon loss of singularity, in the latter case. Other benefits of polycrystalline growth are reduced seeding problems, e.g. due to twinning, and use of larger diameter poly-seeds for pulling massive ingots.

2. Poly-Ingot Compositional Analysis

a. Boron and Phosphorus

The concentrations of boron and phosphorus were determined from electrical resistivity measurements made on single-crystal silicon. The procedure involves first pulling a small-diameter poly-ingot from DAR-Si in a Czochralski machine, as indicated in Figure 5. This ingot was then multiply float zoned leaving sections that

had been zoned from one to seven times. Electrical resistivity measurements made on the various sections provided data for computing the boron and phosphorus concentrations (see Ref. 14 for details). These values were then adjusted to represent the actual concentrations of the impurities in the original SoG-Si ingot.

Boron and phosphorus analyses were performed only on SoG-Si ingots pulled from DAR-Si produced in the experiments indicated in Table 21 due to the amount of work required per analysis. The SoG-Si of highest purity was an ingot pulled from silicon produced during experiment DAR-200-17. The boron concentration was 6.8 ppma (0.12 ohm-cm) and the phosphorus concentration was 0.45 ppma. The data from this experiment were reproduced in two experiments performed after contract termination.

How do the data from experiment DAR-200-17 compare to the specifications suggested for SoG-Si in Table 1? The phosphorus concentration met the suggested maximum specification of 0.5 ppma. The boron concentration of 7 ppma (0.1 ohm-cm), however, exceeds the suggested specification of 2 ppma (0.3 ohm-cm). Since the suggested boron specification is by no means a rigidly determined value, see Section IV.B, it is interesting to compare it to information reported in the literature. Our 0.1 ohm-cm exactly matches the value reported by Green (3) and by Dunbar and Hauser (4) for the doping resistivity giving maximum solar cell efficiency. Iles and Soclof (15), in addition to Fischer and Pschunder (16), indicate solar cell efficiency should peak around 0.3 ohm-cm such that our SoG-Si would produce cells having an output only 94% of maximum. Therefore, even though the silicon from experiment DAR-200-17 did not meet the conservative 0.3 ohm-cm specification, the 0.1 ohm-cm material comes very close to the maximum in cell efficiency versus resistivity data reported by various investigators.

The ultimate test of SoG-Si lies in the quality of the solar cells it can produce (see Section VII). A compositional specification is also required.

Close examination of Table 21 suggests that various reductions in the concentration of boron or phosphorus

TABLE 21. BORON AND PHOSPHORUS ANALYSES OF THE FINAL SoG-Si PRODUCT FROM THE DOW CORNING PROCESS AS PULLED FROM VARIOUS DAR-Si MELTS

DAR RUN NO.	CONC. (ppma)		RAW MATERIALS	
	B	P	CARBON	QUARTZ
50-5	12	13	char., purif.	Ark.
50-6	36	50	char.	Ark.
50-7	24	25	char., purif.	Ark.
50-9	9	12	char., purif.	B.C.
50-11	10	11	char., purif.	B.C.
200-8	16	14	CB9/Starch	Ark.
9	13	9	CB9/Starch	Ark.
10	12	9.7	AC	Ark.
11	14	16	AC	Ark.
12	12	4.5	CB9/Starch	B.C.
13	11	5.4	CB9/Starch	B.C.
14	13	4.5	CB9/Starch	B.C.
15	8.0	4.2	AC	B.C.
16	9.6	5.6	CB9/Sucrose	B.C.
17	6.8	0.45	CB5/Sucrose	B.C.

Note: The resistivity - analyzed boron and phosphorus concentrations in DAR-Si do not necessarily correspond to concentrations in the raw materials because of the limitation of the emission spectroscopic method for carbon and quartz.

might be directly tied to changes in carbon black (CB) or quartz sources of supply. The gradual reductions in impurities were partially due to ever improving methods of clean operation of the DAR, especially during later experiments. The most obvious reduction in phosphorus can be definitely traced to the use of Thermax Stainless carbon black in experiment DAR-200-17. Again, this low concentration of phosphorus in SoG-Si was confirmed by later experiments in the DAR.

b. Other Impurities

Analysis of the final Dow Corning product for impurities other than boron and phosphorus is difficult since the impurities are about equivalent to the concentrations found in semiconductor-grade silicon. An analysis of the SoG-Si ingot at the 50-% point of the silicon pulled from experiment DAR-200-17 is shown in column three of Table 22. The analysis was performed in Dow Corning's spark-source mass spectrometer that has only analyzed pure semiconductor-grade silicon. All indicated impurities in the SoG-Si could not be detected at the 3-30 ppba sensitivity of the instrument, except for sodium which was present at 3 ppba. Nearly identical results are found when analyzing semiconductor silicon; i.e., all impurities analyze to have concentrations lower than their detection limits of 3-30 ppba. Earlier work (10) showed that there was no detectable difference in the purity of the silicon between the 40-% and 65-% amounts of the total silicon pulled. No difference in quality is expected between the 0 to 76-% portions (see next section).

Earlier reported data (10) indicated that a reasonable estimate of impurity concentrations in the SoG-Si ingot could be obtained by multiplying the effective segregation coefficients times the impurity concentrations found in the DAR-Si. The results of this appear in Table 22 where the impurity concentrations (now in ppma) of silicon from experiment DAR-200-17 have been multiplied by the effective segregation coefficients reported in Reference 6. The estimated concentrations are less than the SoG-Si specifications from Table 1 in all instances.

TABLE 22. ANALYSIS OF SoG-Si INGOT FOR IMPURITIES OTHER THAN BORON AND PHOSPHORUS

Impurity (ppma)	E.S. of DAR-Si*	S.S.M.S. of SoG-Si Ingot	Segregation Coeff. Estimate of SoG-Si Ingot from DAR-Si	SoG-Si Specification
Al	70	1**	0.1	0.2
Ca	35	N.A.	-	-
Cr	5	<0.003	6×10^{-5}	4×10^{-3}
Cu	2	<0.015	0.002	0.8
Fe	40	<0.03	3×10^{-4}	6×10^{-3}
Mg	N.A.	<0.005	-	-
Mn	5	<0.003	7×10^{-5}	2×10^{-3}
Mo	5	<0.010	2×10^{-7}	-
Na	N.A.	<0.003	-	-
Ni	5	<0.03	1×10^{-4}	1
Sn	N.A.	<0.005	-	-
Ta	N.A.	<0.010	-	-
Ti	5	<0.005	1×10^{-5}	6×10^{-5}
V	5	<0.003	2×10^{-5}	8×10^{-5}
Zn	N.A.	<0.005	-	-
Zr	5	<0.012	8×10^{-8}	2×10^{-4}

* DAR-200-17

** From resistivity measurements of multiply float-zoned ingot

These low values of impurity concentrations should permit the Dow Corning polycrystalline ingot to meet or exceed any specifications for such impurities in SoG-Si.

3. Poly-Ingot Yield

Polycrystalline ingots were pulled from DAR-Si using a Hamco, Model 800, crystal growth machine. The purpose of the pulls was to establish usable ingot yield in a larger machine since ingot yield has been machine limited at 65% in the smaller NRC equipment.

Silicon from the DAR was loaded into the crystal grower and melted under argon. Slag floating on the silicon surface was totally removed by blowing it to the side of the crucible and freezing it there by carefully lowering the crucible temperature. The slag was predominately silica that had been formed by oxidation of the silicon surface during its removal from the DAR. The weight of the slag as a percentage of the total material charged to the puller was not measured.

Although a single-crystal seed was used to initiate growth, the resulting ingot was always polycrystalline. The ingot surface appeared the same as that of a single crystalline ingot without its longitudinal lines due to the intersection of crystal planes. The bottom 7% of the crystal (see Fig. 5) was feathered due to the onset of constitutional supercooling.

The data in Table 23 indicate that the average yield of total ingot from the charged material was 83%. The usable ingot yield was 77% after the feathered end was cropped. In a later economic analysis, 90-% yield is assumed for a commercial-scale operation.

The data in Table 23 are obviously the result of a very incomplete investigation. It is not clear how much the usable silicon yield can be increased by recharging the feathered end of the ingot nor by decreasing the amount of slag* charged to the puller.

*This is easily done by improving the removal technique of silicon from the DAR. Scale-up would be a significant factor in itself.

TABLE 23. YIELD OF SoG-Si POLY-INGOT FROM DAR-Si USING CZOCHRALSKI PURIFICATION

Si Source DAR-200-	Charge Wt. (g)	Ingot Wt. (g)	Ingot Len. (cm)	Ingot Diam. (cm)	Ingot/Charge (%)	Tang Wt. (g)	(Ingot-Tang)/Charge (%)
16	4556	3780	28	8.9	83	285	77
17	6104	5060	47	7.6	83	448	76

The final Dow Corning product was tested to determine whether it would be a suitable material for a user producing "sheet" material via the Czochralski technique. The SoG-Si poly-ingot was again loaded into a Hamco, Model 800, Czochralski puller. The resulting ingots were always single crystalline and exhibited the same characteristics as ingots pulled from semiconductor-grade silicon, such as lack of seeding problems, good diameter control, and silicon yield.

Second-generation ingots were pulled from the seed and tang ends of the same SoG-Si poly-ingot (see Fig. 5) and showed no difference in pulling characteristics (see above) that might be attributed to different levels of impurity concentrations along the length of the poly-ingot.

C. Bridgman Crystal Growth

1. Experimental

The objective of this technique was to demonstrate the feasibility of segregating impurities during the unidirectional solidification of silicon in a cylindrical form. The approach was to solidify silicon from the bottom to the top of a crucible by controllably decreasing the temperature so that the solid-liquid interface moves upward. The reason for pursuing this technique was that it appears that the furnace equipment should be readily scalable to large-diameter ingots within reasonable capital costs. This is necessary since crystal growth capital represents a major portion of the total cost of producing silicon via the Dow Corning Process.

The Astro, Model 70-240, Gradient Furnace System, as shown in Figure 6, consists of a three-zone, variable temperature-gradient furnace assembly and a retractable work-support hearth. The effective work zone of the furnace is 18-cm diameter x 61-cm long, with the central 41 cm being adjustable from constant temperature to a linear gradient of approximately $9\text{ }^{\circ}\text{C/cm}$, with the support hearth at maximum elevation. Maximum temperature, either with a constant zone or a temperature gradient, is $1700\text{ }^{\circ}\text{C}$. The gradient on the silicon charge can be increased by lowering the hearth into the water-cooled chamber below the furnace. The silicon charge is loaded onto the support hearth with the cooling chamber and support hearth fully lowered. The hearth can be raised or lowered at rates of between 0-13 cm/min and 0-25 cm/h.

The nine experiments carried out by Bridgman solidification are summarized in Table 24. No segregation was observed when purifying MG-Si by the Bridgman technique. This is attributed to the large concentration of impurities in MG-Si that are not mixed into the melt as they are rejected at the solid-melt interface. No forced mixing occurs due to rotation as is the case for Czochralski crystal growth.

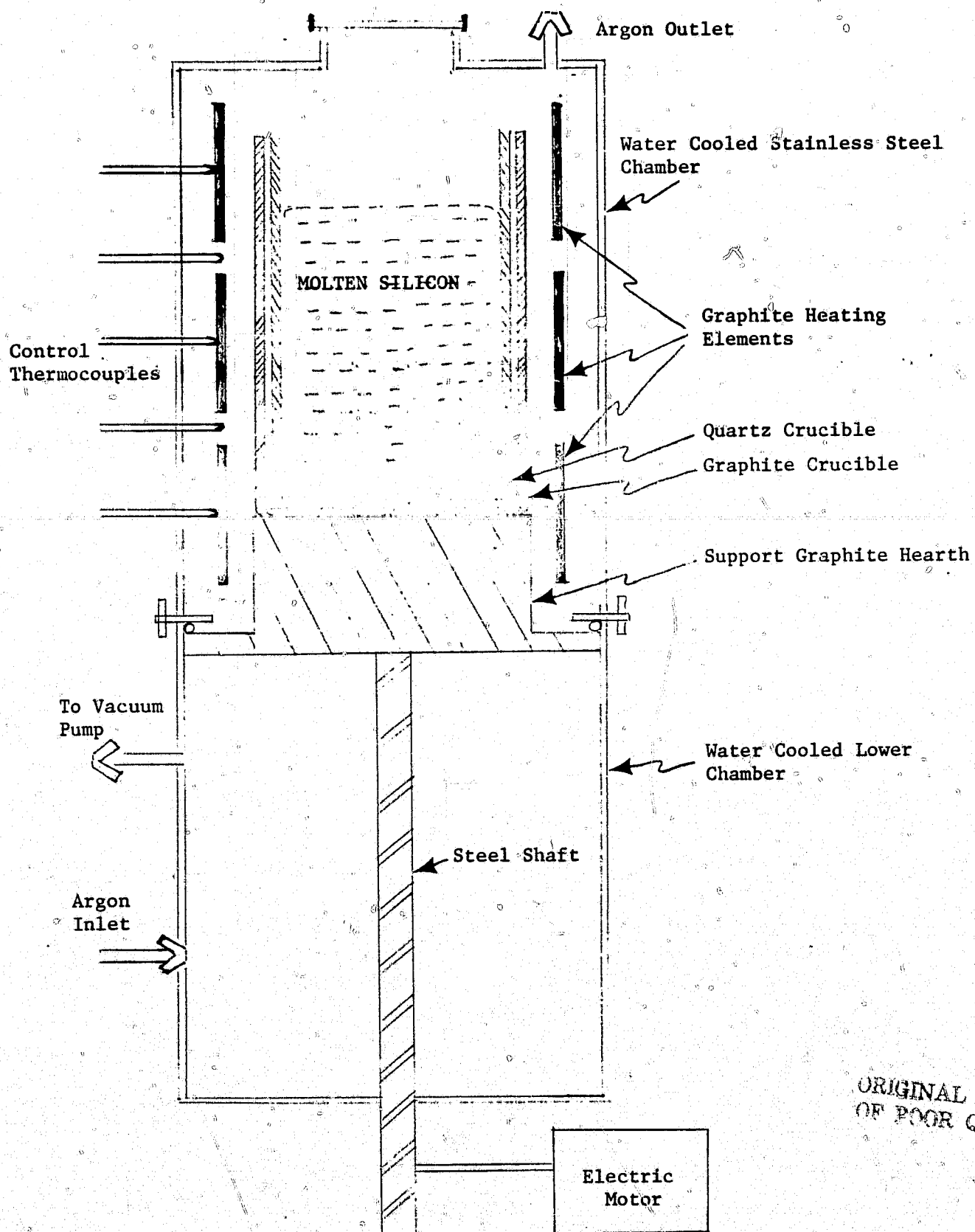


Fig.6 Gradient Furnace Schematic

TABLE 24. BRIDGMAN-TYPE EXPERIMENTS TO SEGREGATE IMPURITIES DURING UNIDIRECTIONAL SOLIDIFICATION

Exper. No.	Si Grade	Dopant/ Conc. (ppba)	Wt. (kg)	Axial Grad. ($^{\circ}\text{C}/\text{cm}$)	Solid. Rate (cm/h)	Cool Rate $^{\circ}\text{C}/\text{h}$	Segregation?
1	MG-Si	-	5.3	3.2	4.4	14	No
2	MG-Si	-	6.4	3.2	4.4	14	No
3	Semi.	B/55	5.0	3.2	4.4	14	?
4	Semi.	Al/ 10^4	5.3	3.1	5.1	16	Yes
5	Semi.	Al/ 10^5	5.9	5.3	3.6	19	Yes
6	Semi.	Al/ 10^5	5.7	5.1	7.1	36	Yes
7	Semi.	Al/ 10^5	5.8	0	5.1	*	Yes
8	Purified met.	-	5.8	0	5.0	*	Yes
9	Purified met.	-	5.6	0	2.5	*	Yes

* Dropped hearth from heater zone to water-cooled zone.

Experiments 3-7 were performed using doped semiconductor silicon in order to more precisely approximate the purity of DAR-Si. Two unidirectional solidification methods were used. In Experiments 3-6, the crucible was maintained in a constant position while the temperature was decreased while maintaining an 100 °C temperature gradient across the 30-cm length of the silicon. For Experiment 7, the crucible was dropped out of a constant-temperature zone into a H₂O-cooled zone of much lower temperature. The silicon mass, temperature gradient, and the rates of cooling and solidification are provided in Table 24.

Segregation of boron in Experiment 3 was not obvious due to the high segregation coefficient of boron (0.8). Effective segregation of aluminum, however, was apparent in the later experiments due to its more favorable segregation coefficient of about 0.002. Aluminum was used as a dopant in order to simulate the effectiveness of reducing the concentration of metals that have even lower segregation coefficients. Aluminum doping is most convenient since its concentration can be calculated along the length of the ingot from resistivity measurements made on large grains.

The general experimental procedure was to heat the silicon charge over a 6-hour period until it was 1550 °C at the top of the melt and 1450 °C at the bottom. The temperature was then dropped over 14 hours to 1350 °C at the top of the ingot. The temperature gradient was then decreased to zero and the ingot cooled to room temperature in 24 hours. The total elapsed time was about 45 hours. In the case of Experiment 7, the melt was maintained at 1550 °C for 3 hours after the initial 6-hour heat-up. The crucible was then dropped at 5 cm/h. Total elapsed time was 24 hours. The ingot, upon removal from the quartz crucible, was some times found to be one piece and some times to be cracked. No efforts were made to investigate cracking.



Figure 7. Photograph of Grain Structure in Bridgman-Solidified Silicon Ingot (Scale in mm).

ORIGINAL PAGE IS
OF POOR QUALITY

The ingot was then sawed in half along its axis, etched in KOH to enhance grain structure (see Figure 7), sand blasted along a strip running up the ingot axis, and finally the resistivity was measured incrementally along the strip.

The effects of aluminum segregation along the solidified ingots are shown in Figure 8 for Experiments 4, 5, and 7 (the ingot from Experiment 6 cracked severely due to loss of furnace power). The segregation of aluminum from the bottom to the top of the ingot is obvious in all cases. The data for Experiment 5 lie approximately one order-of-magnitude higher than Experiment 4, in agreement with the initial aluminum doping levels of 100 ppm and 10 ppm, respectively. The shape of both curves agree in general with the shape of the theoretical curve (see Figure 8) which was calculated from

$$C = k C_0 (1-X)^{k-1}$$

where the concentration, C , is a function of the initial concentration, C_0 , the segregation coefficient, k , and the fractional part of the melt to freeze, X .

Dropping the hearth from the heater zone to the water-cooled zone apparently yields more efficient segregation of aluminum.

Two crack-free ingots, 9-cm in diameter and 13-cm high, were grown from upgraded arc-furnace silicon. For the ingot grown at a rate of 5 cm/h (720 g/h), the major impurities of Fe and Al started to appear at the 36-% point. In case of the ingot grown at 2.5 cm/h (320 g/h), impurities started to appear at the 49-% point. The low yield of purified silicon is considered to be due to impurity trapping at the grain boundaries of the polycrystalline ingot and to excessive impurity build-up at the solid-liquid interface.

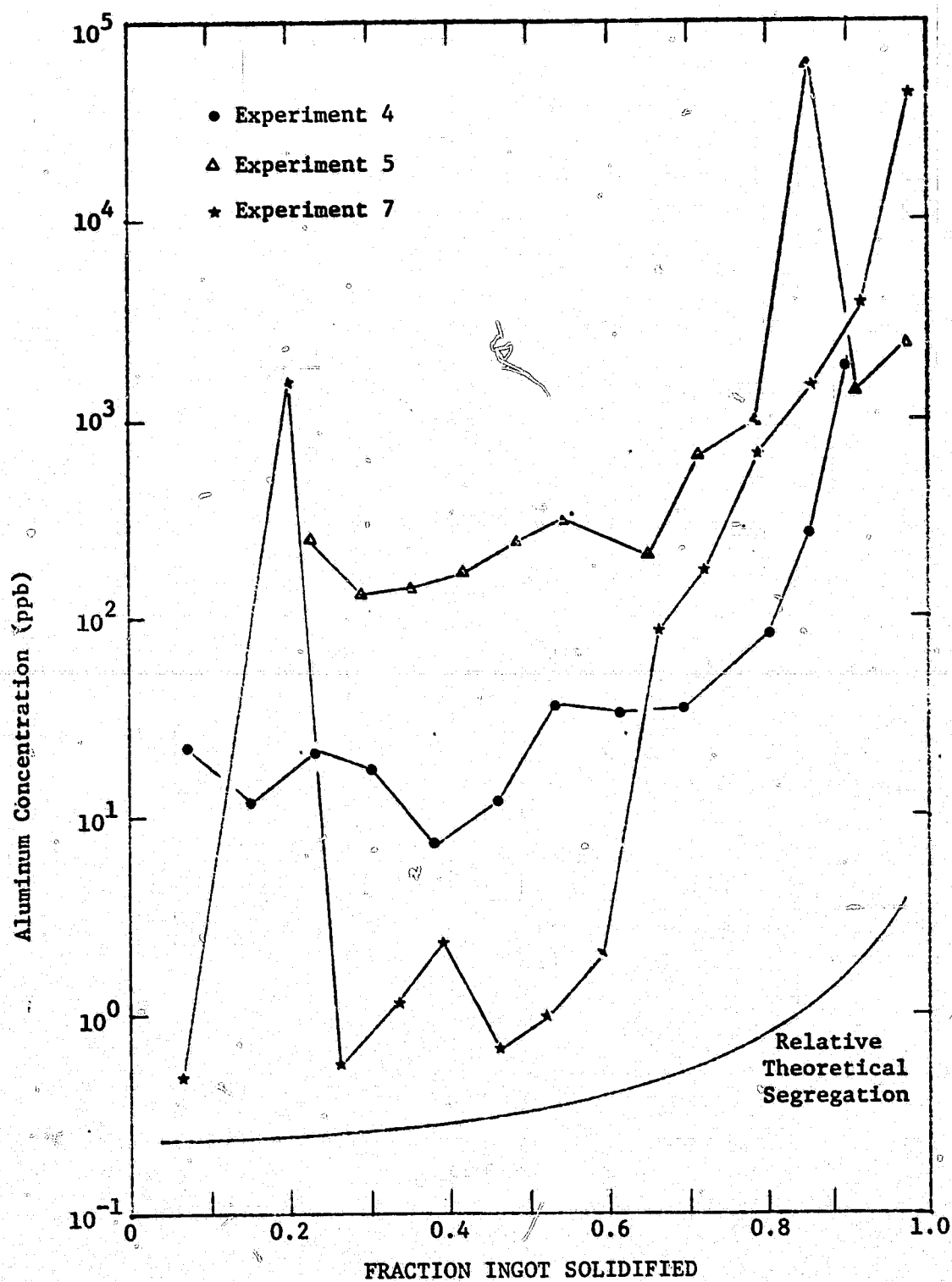


Figure 8. Effect of Segregation on Aluminum Concentration During Bridgman-type Solidification.

2. Cost Analysis

Detailed cost analyses were carried out, in 1975 dollars, for two different growth rates at ingot diameters of 25, 30 and 50 cm (7). The corresponding crucible capacities considered were 45, 81, and 450 kg of silicon. Cost numbers were calculated based on the following assumptions:

- DAR-Si can be effectively purified by the Bridgman-type process to yield 90-% usable silicon.
- Installed capital cost for the process was estimated at 2.5 times the equipment cost and depreciated over a period of seven years.
- Furnace cool-down, clean-up and maintenance was considered to be 20% of the total growth cycle.
- Power consumption was estimated at 25 kWh/kg Si for a 45-kg charge and 20 kWh/kg for a 450-kg charge. The power cost was estimated at \$0.025/kWh.

The weight of the silicon charge and rate of the ingot growth were the two single most important factors which affected the cost of the purified silicon. The power consumption was also a significant cost item. At a growth rate of 5 cm/h using a silicon charge weighing 45 kg, the purification cost was calculated to be \$3.96/kg silicon. At a higher growth rate of 11.5 cm/h from a 450-kg crucible charge, silicon could be purified at a cost as low as \$1.48/kg Si, assuming all technical assumptions could be met.

3. Conclusions

The Bridgman technique of purifying DAR-Si was discontinued due to limited funds. The choice was made to continue crystal growth purification using the Czochralski technique due to its much higher degree of technical sophistication. In the long-range, however, further development of Bridgman purification technology is recommended since it could result in lower-cost SoG-Si.

D. Vacuum Evaporation

1. Background

It was suggested by JPL that Dow Corning attempt to purify silicon via evaporation of impurities under vacuum, as indicated by Bradshaw and Mlavsky (17). To explore the feasibility of significantly decreasing the concentration of impurities in MG-Si by vacuum evaporation, an NRC, Model 2805, crystal puller was modified for vacuum operation. This unit permitted up to 12-hour operation at pressures in the range of $0.1\text{--}1 \times 10^{-3}$ Torr. The pressure selected for experimental investigation was $0.2\text{--}0.4 \times 10^{-3}$ Torr range. Experimental pressures were chosen to be slightly above the vapor pressure of silicon at the particular melt temperature under study, thereby avoiding excessive loss of silicon which could result in actual concentration of impurities in the melt.

2. Experimental Procedure

A sample of MG-Si was placed in a quartz crucible and loaded into the furnace. In the first experiment, the surface area of the molten silicon was 60 cm^2 while the mass of the silicon charge was 450 g, providing an area-to-mass ratio of $0.13\text{ cm}^2/\text{g}$. After loading, the furnace was purged with argon and the charge was melted under an argon atmosphere (1 atm). Once molten, a silicon sample was withdrawn to provide a specimen for base-line impurity analysis. The chamber was then evacuated. Every three hours the furnace was back-filled with argon and the melt was resampled.

3. Results

Three experiments were performed using different silicon area-to-mass ratios. Emission spectroscopic analyses of silicon sampled at 0, 3, and 6-hour intervals appear in Table 25. No reduction in the concentration of any impurity element is discernable.

TABLE 25. IMPURITY ANALYSES OF SILICON SUBJECTED TO VACUUM EVAPORATION FOR VARIOUS TIME PERIODS.

Impurity (ppmw)	TIME UNDER VACUUM (h)								
	A/M = 0.13 cm ² /g			A/M = 0.30 cm ² /g			A/M = 0.44 cm ² /g		
	0	3	6	0	3	6	0	3	6
Al	1200	1300	950	2900	1400	1900	420	600	780
As	<100	<100	<100	<100	<100	<100	<100	<100	<100
B	60	100	75	57	53	56	24	20	29
Ca	-	-	-	<10	50	<10	<10	<10	<10
Cr	170	170	150	260	180	210	110	180	190
Cu	80	80	80	50	40	40	80	80	80
Fe	3000	4200	3000	5400	4700	5200	2800	3500	4300
Mn	120	160	100	110	80	100	50	80	80
Ni	80	100	70	120	80	110	80	90	100
P	19	20	17	20	20	10	20	20	20
Sb	<50	<50	<50	<50	<50	<50	<100	<100	<100
Sn	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ti	360	480	330	360	280	330	250	320	380
V	160	190	130	130	120	130	140	170	200
Zr	20	20	20	50	40	60	20	20	20

The variation in individual impurity analyses over a 6-h interval is well within the error of the analytical technique. The concentrations of the volatile impurities As, Ca, Sb, and Sn were below their detection limits. This is most likely due to the high temperatures MG-Si is subjected to during its arc-furnace production.

The silicon in the experiment performed at the area-to-mass ratio of 0.44 g/cm^2 had a layer thickness of 0.7 cm. This was the minimum thickness attainable due to the surface tension of the MG-Si.

It was recommended that further work on MG-Si purification via vacuum evaporation be discontinued. This recommendation was made on the fact that absolutely no evidence had been obtained suggesting any degree of MG-Si purity improvement. Any continued effort aimed at significantly increasing the surface area-to-mass ratio would pose both experimental and practical problems of concern for the viability of a vacuum evaporation process. This is due to difficulties associated with heating and containing large, thin layers of molten silicon without excessive energy usage and silicon contamination.

VII. EVALUATION OF SOG-SI AS SOLAR CELLS

Proper choice of raw materials allowed DAR-Si to be produced with low boron (7 ppma) and phosphorus (0.5 ppma) concentrations during only the last two months of the contract. This DAR-Si was further processed, as indicated below, and supplied to two companies for limited evaluation as solar cells.

Silicon from experiment DAR-200-17 was purified in a Czochralski puller to produce polycrystalline SoG-Si. This material was then converted into single-crystalline (100) silicon via a second Czochralski pull. The ingot ranged in resistivity from 0.19 ohm-cm at the seed end to 0.18 ohm-cm at the tang end. Single-crystalline ingots were supplied to Applied Solar Energy Corp. (OCLI) and to ARCO Solar Inc. for sawing into wafers and cell fabrication.

Applied Solar Energy Corporation fabricated (18) twelve solar cells on wafers cut from the seed half of the 3-cm-diameter ingot. Values for electrical parameters for the individual cells are provided in Table 26. Air-mass-zero efficiencies after a SiO antireflection coating ranged from 7.2 to 10.5%, the average being 9.3%. This value is 82% of control cells fabricated from 2 ohm-cm semiconductor silicon. Other average electrical parameters were $V_{oc}=599$ mV, $I_{sc}=124$ mA and CFF=67%. Applied Solar Energy Corporation estimated the average AM1 efficiency to be 10.6%, assuming no limitation due to minority carrier diffusion length.

Very limited solar cell data were provided by ARCO Solar, Inc. on wafers cut from the tang half of the same 3-cm-diameter ingot. A standard process was used to produce 24 cells the output of which translated to AM1 efficiencies between 10.5 to 13.4% when AR coated (19,20).

Enhanced solar cell processing (18) by Applied Solar Energy Corporation did not significantly improve cell performance. However, ARCO Solar was able to push cell efficiencies to greater than 14% (AM1, AR coated) by using enhanced processing (21).

Table 26. Solar Cell Data from Applied Solar Energy Corporation for Cells Fabricated from Wafers from Czochralski Ingots Pulled from SoG-Si (DAR-200-17).

Cell No.	V _{oc}	I _{sc}	P _{max}	CFF	MEASURED η (AMO)	ESTIMATED η (AMI)
	mV	mA	mW	%	%	%
1	609	127	56.6	73	10.5	12.0
2	588	123	40.9	56	7.6	8.7
3	608	125	56.6	74	10.5	12.0
4	597	124	48.1	65	8.9	10.1
5	607	124	55.3	73	10.2	11.6
6	604	124	54.2	72	10.0	11.4
7	586	122	38.9	54	7.2	8.2
8	598	126	50.6	67	9.4	10.7
9	601	126	52.2	69	9.7	11.1
10	600	122	51.8	71	9.6	10.9
11	593	126	47.0	63	8.7	9.9
12	598	123	48.0	65	8.9	10.1
Aver.	599	124	50.0	67	9.3	10.6
*Control	595	132-136	60	76	11.2-11.6	12.8-13.2

* Typical for 2 ohm-cm

VIII. THE DOW CORNING PROCESS

A. Preliminary Process Flow Diagram

A preliminary PFD was developed based upon the basic process outlined in Figure 1: raw materials feeding a commercial arc furnace that subsequently yields DAR-Si lumps that are charged to Czochralski pullers. The polycrystalline ingots from the puller are the final SoG-Si product from the Dow Corning Process.

The PFD in Figure 9 is comparatively simple compared to that of PFD's prepared for most chemical plants. The PFD is based upon the output of 1 kg of SoG-Si. Quartz sizing is assumed to result in a 5% loss of SiO_2 .

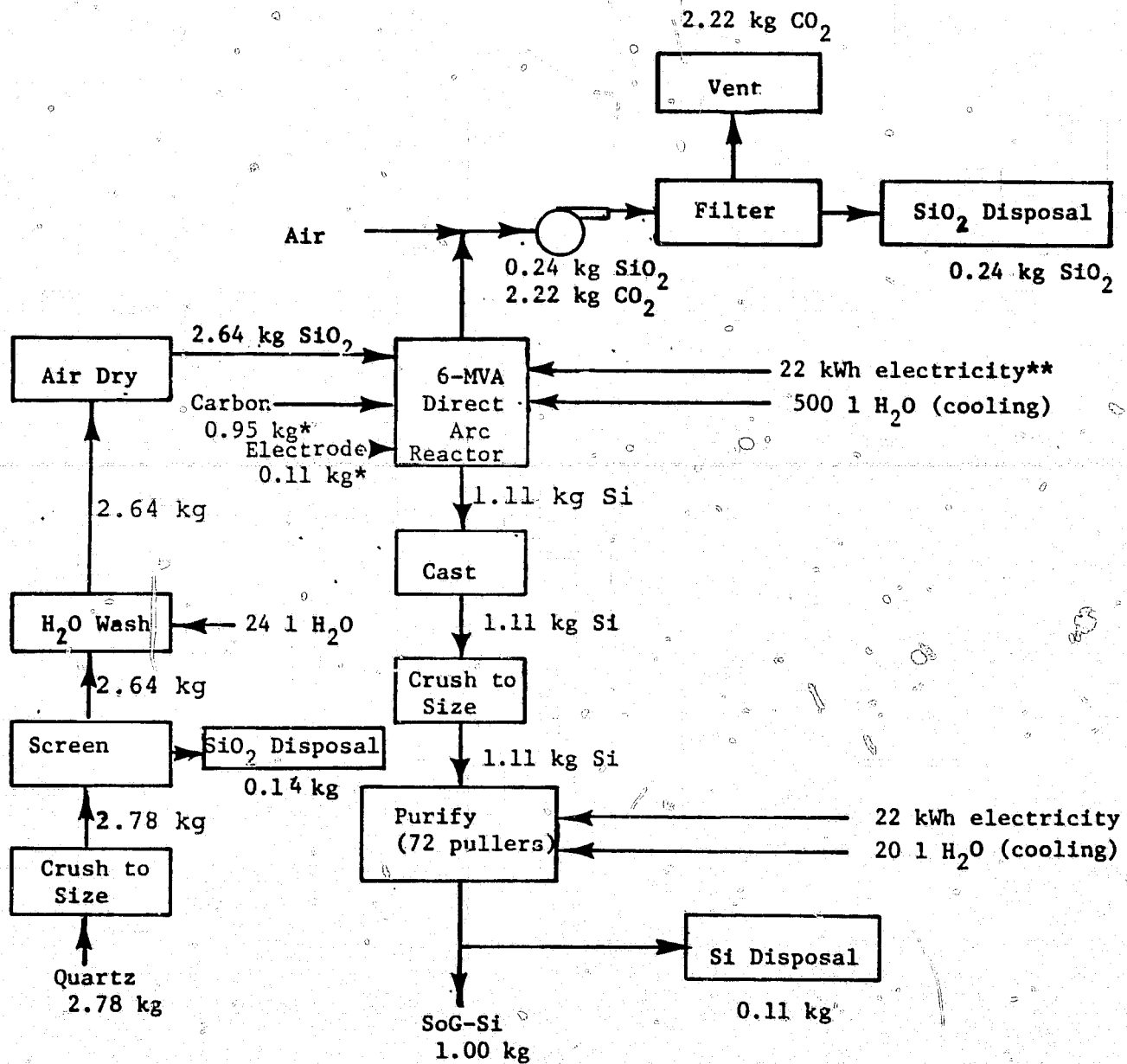
The DAR is a 6-MVA unit cost estimated by Elkem-Spigerverket A/S for producing 3000 MT/y of silicon. A 80-% conversion of SiO_2 to Si (based on Si) is typical of a commercial unit today. The 20-% Si loss is via SiO gas that is air oxidized to SiO_2 dust at the furnace top and removed in a baghouse down stream. Electrical consumption of 22 kWh/kg is based upon actual data experienced in the industry for producing MG-Si.

Silicon from the 6-MVA DAR is cast, crushed to size, and loaded into Czochralski pullers capable of continuously pulling 30-cm-diameter polycrystalline ingots of SoG-Si. In this case, 72 pullers would be required for a 3000 MT/y rate with a 90-% ingot yield. The following section discusses the trade-off in final SoG-Si cost versus ingot diameter. Electrical energy consumption is based upon experience and projections by Hamco, Leybolt-Hereaus, and Varian.

B. Preliminary Cost Analysis

A preliminary cost analysis of the Dow Corning Process was put together from two main sources of data. The first source was a cost estimate prepared by Elkem-Spigerverket A/S for a 6-MVA arc furnace. Their estimates are based on

FIGURE 9. PRELIMINARY PROCESS FLOW DIAGRAM FOR A 3000-METRIC-TON-PER-YEAR SOLAR SILICON PLANT



* 100-% fixed carbon

** 16 kWh/kg: DAR
 4 kWh/kg: Services and Environmental Control
 20 kWh/kg Si

experience of supplying furnaces of this size to the metallurgical industry.

The second source of data was that regarding the cost of Czochralski pullers today. Discussions were carried out with Hamco, Leybolt-Hereaus, and Varian regarding the simpler machine required by the Dow Corning Process and their projections of producing equipment capable of pulling 30-cm ingots continuously.

The preliminary cost analysis was carried out in a manner similar to that done by Prof. Yaws of Lamar University in his comparison of various processes for producing silicon. Estimate of installed capital of \$37.7 M (million) was calculated as being equal to three times the cost of purchased equipment (see Figure 10). The purchased equipment is broken down by silicon production (DAR, recovery, and auxiliary equipment) and silicon purification (Czochralski pullers) steps. The pullers represent 79% of total purchased equipment costs.

The preliminary cost analysis in Figure 11 shows the total manufacturing cost of \$6.56/kg Si to be composed of \$4.57/kg of direct cost and \$1.99/kg of indirect cost. An added general expense of 15% brings the total SoG-Si cost to \$7.54/kg Si (no profit, 1975 dollars).

A series of options are available for the purification step. The effect of these options on the final SoG-Si product cost is given in Figure 12. The final cost is shown as a function of ingot diameter for various ingot yields as well as pulling techniques. A much more conservative cost analysis for continuous pulling of 15-cm-diameter polycrystalline ingots at an 80-% yield, shows that the final, estimated cost of SoG-Si to be about \$11.70/kg Si. This approach uses present-day technology and requires very little developmental effort in Czochralski technology.

A more detailed breakdown of the actual information used to generate the estimated cost analysis in Figure 11

<u>PURCHASED EQUIPMENT</u>	<u>COST (\$M)</u>
1. Direct Arc Reactor (DAR)	1.38
2. Silica Recovery System	0.32
3. Auxiliary DAR Equipment	0.97
4. 30-cm ingot pullers (72)	<u>9.90</u>
	12.57

Installed Capital = 3 times purchased equipment
= \$37.71 M

Figure 10. Estimated Installed Capital (1975 Dollars)
for Producing 3000 MT/y of SoG-Si Via the
Dow Corning Process

1. Direct Manufacturing Cost	
A. Raw Materials	\$1.15/kg Si
B. Labor (37@ \$6.90/h + 50% O.H.)	0.27
(9@ \$4.90/h + 50% O.H.)	0.05
C. Utilities (\$0.03/kWh)	1.26
D. Maintenance (10% of installed capital)	1.26
E. Expendables	<u>0.58</u>
	4.57
2. Indirect Manufacturing Costs	
A. Depreciation (Pullers over 7 y)	1.41
(other over 12 y)	0.20
B. Taxes and Insurance (3% of capital)	<u>0.38</u>
	1.99
3. Total Manufacturing Cost (1+2)	6.56
4. General Expenses (15% of 3)	0.98
5. Total SoG-Si Cost (no profit)	\$7.54/kg Si
6. SoG-Si Price (*)	\$12.15/kgSi

Figure 11. Total Estimated Price (1980 Dollars, with Profit)
of SoG-Si for Producing 3000 MT/y Via the Dow
Corning Process

(*) Price was calculated using a tax rate of 46% and a return on investment of 20%. A working capital of 15% was also added on top of the fixed capital.

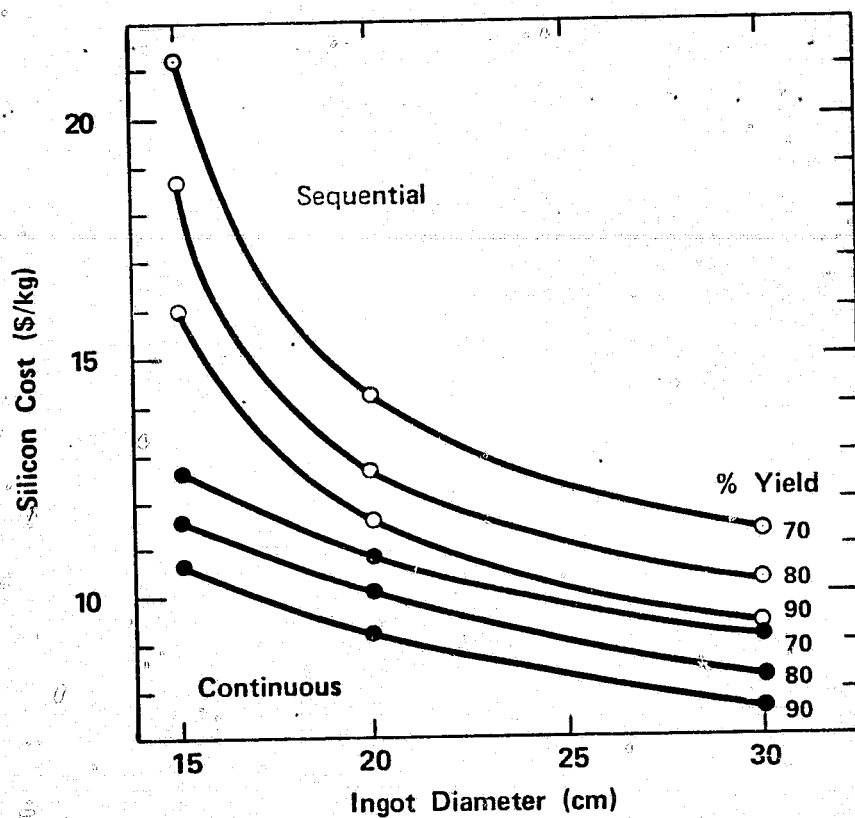


Fig. 12. Variation of SoG-Si Cost (1975 \$'s and no Profit) with Ingot Diameter and Silicon Yield

is provided in Figures 13 and 14. Shown is a slightly different cost estimate in which the overall Dow Corning Process is broken down into its two major steps which are considered to take place in separate plants. First is a cost estimate for a plant to produce 3300 MT/Y of DAR-Si. The second plant takes the DAR-Si and converts it to SoG-Si. This approach to the overall cost analysis differs very little in the final cost when compared to the integrated-plant approach. It does provide a mechanism, however, of more clearly indicating individual step contributions to cost. Further information regarding Czochralski purification data can be found in Reference 7.

Again, the major capital cost relates to Czochralski crystal growth. A lower-cost crystal growth technique could reduce manufacturing cost and capital expenditure significantly.

C. Energy Analysis

A complete energy analysis from raw materials to finished solar array has been presented by Hunt (22) going the semiconductor silicon route. An estimate was made (22) of the total energy expended in using the Dow Corning Process for silicon rather than the semiconductor silicon process. The component parts of this are the energy required to produce DAR-Si and the energy necessary to convert it to SoG-Si via one Czochralski pull.

The energy to produce DAR-Si is nearly identical to that for MG-Si production, i.e., 24 kWh(e)/kg Si. The energy to produce 1 kg of Czochralski ingot is 110 kWh(e)/kg Si (18). If one assumes a 90-% yield of SoG-Si from DAR-Si total energy consumption is

$$\begin{aligned} E &= E_{\text{DAR-Si}}/0.90 + E_{\text{CZO}} \\ &= 24/0.90 + 110 \\ &= 137 \text{ kWh(e)/kg Si} \end{aligned}$$

This corresponds to a 5.3-month payback time assuming a 12-%, Aml cell, illuminated by 100 mW/Cm² during a 5-hour day. This is for a 100-mm-diameter, 200-μm-thick cell containing 3.6g of silicon.

The above analysis included the energy associated with raw materials used in the DAR-Si process (18).

Capital Cost

<u>Purchased Equipment</u>	<u>Cost (\$M)</u>
Reactor (6MVA)	1.38
Recovery System	0.32
Auxiliary Equipment	<u>0.97</u>

2.67

Installed Capital = 3 times purchased equipment
= \$8.0 M

Manufacturing Cost

1. Fixed Cost			<u>\$/kg Si</u>	
A. Labor (13@ \$6.90/h + 50% O.H.)			0.09	
	(9@ \$4.90/h + 50% O.H.)		0.05	
B. Maintenance (10% of \$8.0 M)			0.24	
C. Depreciation (12-year)			0.20	
D. Taxes and Insurance (3% of \$8.0M)			<u>0.07</u>	
				0.64
2. Variable Cost	<u>kg/kg Si</u>	<u>\$/kg</u>	<u>\$/kg Si</u>	
A. Quartz	2.50	0.20	0.50	
B. Carbon Black Pellets*	0.86	0.51	0.44	
C. Electrodes	0.10	1.00	0.10	
D. Electric Energy	20 kWh/kg	\$0.03/kWh	<u>0.60</u>	
				1.64
3. Total Manufacturing Cost (1&2)				2.28

* 100-% fixed carbon basis

Figure 13. Total Estimated Cost (1975 Dollar, no Profit)
for Producing 3300 MT/y of DAR-Si

Capital Cost

Purchased Equipment

72 Machines

Cost (\$M)

9.9

Installed Capital = 3 times purchased equipment
= \$29.7 M

Manufacturing Cost

1. Fixed Cost

\$/kg

A. Labor (24@ \$6.90/h + 50% O.H.)

0.17

B. Maintenance (10% of \$29.7 M)

0.99

C. Depreciation (7 year)

1.41

D. Taxes and Interest (3% of \$29.7 M)

0.30

2.87

2. Variable Cost

A. DAR Silicon 1.11 kg/kg Si

\$2.28/kg

2.53

B. Expendables

0.58

C. Electric Energy 22 kWh/kg Si

\$0.03/kWh

0.66

3.77

3. Total Manufacturing Cost (1+2)

6.64

4. General Expenses (15% of 3)

0.99

5. Total Cost of Product (no profit)

7.63

Figure 14. Total Estimated Cost (1975 Dollars, no Profit)
for Producing 3000 MT/y of SoG-Si from a DAR-Si Plant

IX. CONCLUSIONS

- The technical feasibility of the Dow Corning Process has been demonstrated for the high-volume production of solar-cell-grade silicon.
- Raw materials are commercially available that meet the volume goal for SoG-Si.
- Low-cost raw materials represent only 12% of the \$10/kg price goal.
- Special commercially-available raw materials were identified which were reactive in the Direct Arc Reactor and which were pure enough to produce silicon that could be fabricated into reasonably efficient solar cells.
- Silicon can be continuously produced in a Direct Arc Reactor.
- The concentration of impurities in silicon from the Direct Arc Reactor are low enough so that further purification of the silicon can be effected via segregation during crystal growth except for B & P.
- Technology exists in the metallurgical industry for scaling up the DAR process to any reasonable scale desired.
- Silicon from the DAR can be effectively purified by Czochralski crystal growth to produce a polycrystalline ingot with non-doping metal impurity concentrations equivalent to semiconductor silicon.
- The lowest boron concentration in the SoG-Si ingot attained within the scope of this contract is 7 ppma (0.12 ohm-cm), with phosphorus compensation of less than 10% of the boron concentration.
- Single crystalline silicon ingots can be produced directly from polycrystalline SoG-Si using standard Czochralski crystal growth technology.

- A limited number of solar cells produced on such single crystalline silicon have demonstrated conversion efficiencies ranging from a low of 7.2% (AMO, AR) to a high of >14% (AM1, AR).
- At a 3300-MT/y rate, DAR-Si can be produced for a cost of \$2.28/kg (1975 dollars, no profit). Advanced CZO technology could result in SoG-Si costing \$7.54/kg.
- The Dow Corning Process would require only a 5-month payback time using solar cells to replenish the energy used in silicon production. The energy-use analysis includes the energy equivalent consumed in all raw materials and associated processing.

X. RECOMMENDATIONS

Further development of the Dow Corning Process for SoG-Si should continue at a pilot-plant scale based upon (1) the technical success demonstrated during this contract, (2) the very low-cost potential for the final product, and (3) the commercially-available technology already existing in industry that can be directly applied to the scale-up of the two process steps.

Pilot-plant-scale development must address two objectives: (1) demonstration of technological feasibility on a scale and level of sophistication more closely approximating that of an actual plant; and (2) production of SoG-Si at a scale that will provide silicon at a cost low enough to allow the array manufacturer to drop his price, thereby opening markets for new applications. This will complete the circle by causing greater demand for silicon such that its price will drop further due to increased volume of production.

The remaining recommendations address details that must be accomplished for process scale-up.

- A reliable analytical technique is required as a quality assurance tool for determining boron and phosphorus in quartz and carbon to a lower limit of about 0.1 ppmw. Analytical methods are not sufficient at the 1 ppmw level.
- Quartz sand, which is purer in boron than vein quartz, should be examined as a better source of silica for the carbothermic reduction process.
- Greater control must be obtained over the production of carbon black pellets. This should be done either in-house by the DAR-Si producer or directly at the manufacturer of carbon black itself.
- More sophisticated handling of raw materials must be developed at the DAR-Si pilot plant.

- Large-diameter Czochralski-pulling technology must be developed if the required cost for SoG-Si need be considerably lower than \$10/kg (1975 dollars).
- Alternative processing of DAR-Si should be investigated. Crystal growth methods such as Bridgman or the Heat-Exchanger-Method* are less technologically developed for silicon but they do offer possible cost advantages.
- Much more thorough evaluation is required of silicon in terms of solar cell performance.
- DAR-Si and its purified SoG-Si form should be tested for fabrication into polycrystalline or multicrystalline solar cells using casting techniques such as Heliotronic's Silso Process.

* Crystal Systems Incorporated, Salem, MA.

XI. REFERENCES

1. "Project Quarterly Report-7", Department of Energy Report DOE/JPL-1012-78/13 [DOE Technical Information Center] (1978); prepared by the Jet Propulsion Laboratory for the DOE.
2. F.A. Lindholm, "Studies of Silicon P-N Junction Solar Cells", NASA Report N76-13596, [NTIS] (1975); prepared for NASA by the U. of Florida.
3. M.A. Green, "Resistivity Dependence of Silicon Solar Cell Efficiency and Its Enhancement Using a Heavily Doped Back Contact Region", IEEE Transaction, ED-23 (1976).
4. P.M. Dunbar and J.R. Hauser, "A Study of Efficiency in Low Resistivity Silicon Solar Cells", Solid-State Electronics, 19, 95 (1976).
5. E.S. Rittner, "Improved Theory of the Silicon P-N Junction Solar Cell", J. Energy, 1, 9 (1977).
6. R.H. Hopkins, J.R. Davis, P.D. Blais, A. Rohatgi, R.B. Campbell, P. Rai-Choudhury, R.E. Stapleton, H.C. Mollenkopf, and J.R. McCormick, "Effect of Impurities and Processing of Silicon Solar Cells", Quarterly Report No. 15. Department of Energy Report DOE/JPL-954331-79/7 [DOE Technical Information Center] (1979); prepared by Westinghouse Electric Corp. for the Jet Propulsion Laboratory.
7. L.P. Hunt, V.D. Dosaj, and J.R. McCormick, "Solar Silicon Via Improved and Expanded Metallurgical Silicon Technology", Quarterly Report No. 4, Department of Energy Report ERDA/JPL-954559-77/2 [DOE Technical Information Center] (1977); prepared by Dow Corning Corp. for the Jet Propulsion Laboratory.
8. E.D. Kolb, K. Nassau, R.A. Laudise, E.E. Simpson, and K.M. Kroupa, "New Sources of Quartz Nutrient for the Hydrothermal Growth of Quartz", J. Crystal Growth, 36, 93 (1976).
9. L.P. Hunt, V.D. Dosaj, and J.R. McCormick, loc. cit., Quarterly Report No. 2 (ERDA/JPL-954559-76/2).
10. Ibid., Quarterly Report No. 3 (ERDA/JPL-954559-77/1).
11. J.K. Tuset and O. Raaness, "Reactivity of Reduction Materials for the Production of Silicon, Silicon-Rich Ferroalloys and Silicon Carbide", Electric Furnace Proceedings, 34, 101 (1976).

12. V.D. Dosaj, L.P. Hunt, and A. Schei, "High-Purity Silicon for Solar Cell Applications", J. Metals, 30, 8 (1978).
13. L.P. Hunt and V.D. Dosaj, "Solar Silicon Via the Dow Corning Process", Quarterly Report No. 8, Department of Energy Report DOE/JPL-954559-78/6 [DOE Technical Information Center] (1978); prepared by Dow Corning Corp. for the Jet Propulsion Laboratory.
14. M.C. Arst, et al., "Exploratory Development on Silicon Material for LADIR", Final Report, Air Force Materials Laboratory Report AFML-TR-76-125 (1978); prepared by Rockwell International.
15. P.A. Iles and S.I. Soclof, "Effect of Impurity Doping Concentration on Solar Cell Output", Record 11th IEEE Photovoltaic Specialists Conference, p. 19, Institute of Electrical and Electronic Engineers, New York (1975).
16. H. Fischer and W. Pschunder, "Impact of Material and Junction Properties on Silicon Solar Cell Efficiency", Ibid, p. 25.
17. S.E. Bradshaw and H.E. Mlavsky, J. Electronics, 2, 134 (1956).
18. H.I. Yoo, P.A. Iles, and D.P. Tanner, "Silicon Solar Cell Process Development, Fabrication and Analysis", Annual Report (Phase I), Department of Energy Report DOE/JPL-955089-79/4 [DOE Technical Information Center] (1979); prepared by Optical Coating Laboratory, Inc. for the Jet Propulsion Laboratory.
19. K. Radisavljevic, private communication (February, 1979).
20. C. Gay, private communication (February, 1979).
21. G. Wakefield, private communication (May, 1979).
22. L.P. Hunt, "Total Energy Use in the Production of Silicon Solar Cells from Raw Materials to Finished Product", Record 12th IEEE Photovoltaic Specialists Conference, p. 347, Institute of Electrical and Electronic Engineers, New York (1977).

XII. ACKNOWLEDGEMENTS

The following Dow Corning employees made significant contributions to the work performed under this contract: N. Deitering, L. Ellis, D. Fleet, J. Henige, M. Lovay, R. Moore, and R. Westover, and especially L. Crossman, C. Hendershot, J. McCormick and A. Rauchholz.

In the area of raw material identification, selection, and preparation, recognize F. Charmichael, J. Cline, N. Keyser, W. Merlath, and A. Winker of Interlake, Inc.; L. Joó and F. Miller of Great Lakes Research Corporation; and R. Hinkle of Mars Mineral Corporation.

We extend our appreciation to Elkem-Spigerverket A/S for their assistance in bringing us successfully into the field of arc furnace technology for producing silicon, especially to K. Larsen and A. Schei.

We also thank ARCO Solar Inc. and P. Iles and H. Yoo of Applied Solar Energy Corporation for solar cell evaluations.

XIII. APPENDICES

APPENDIX A1. IMPURITY ANALYSES OF ARKANSAS CLEAR QUARTZ

Impurity (ppmw)	Sample Number						Average
	87	90	549	550	611	629	
Al	10	10	40	20	-	-	20
B	<1	<1	<1	<1	<1	<1	<1
Ca	<10	<10	-	-	-	-	<10
Cr	<10	<10	-	-	-	-	<10
Cu	<5	<5	-	-	-	-	<5
Fe	10	<10	<10	<20	-	-	<10
Mg	<5	<5	-	-	-	-	<5
Mn	<10	<10	-	-	-	-	<10
Ni	<10	<10	-	-	-	-	<10
P	<10	<10	<10	<10	19	<1	<10
Ti	<10	<10	-	-	-	-	<10
V	<10	<10	-	-	-	-	<10
Zr	<10	<10	-	-	-	-	<10

APPENDIX A2. IMPURITY ANALYSES OF ARKANSAS SEMI-CLEAR QUARTZ

Impurity (ppmw)	Sample Number												Average+
	67	88	91	116	117	118	119	120	121	155	156	157	
Al	10	10	10	40	150*	50	40	20	350*	790*	950*	850*	40
B	8	<1	<1	<1	<1	<1	<1	<1	2	2	5	6	3
Ca	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cr	20	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cu	<5	<5	<5	<5	<5	<5	<5	<5	<5	<10	<10	<10	<5
Fe	50	20	<10	40	40	20	30	30	170 ⁺	<10	<10	<50	20
Mg	<10	<5	<5	<5	<5	<5	<5	<5	<5	<10	<10	<10	<5
Mn	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ni	10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
P	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ti	<10	<10	<10	<10	<10	<10	<10	<10	20	<10	<10	<10	<10
V	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zr	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

Impurity (ppmw)	Sample Number													
	281	283	284	285	286	287	395	396	455	456	457	458	610	628
Al	20	20	10	<10	<10	20	50	30	60	70	90	80	-	-
B	5	4	4	3	5	8	2	2	1	3	2	2	3	1
Fe	<10	<10	<10	<10	<10	20	50	50	10	10	20	30	-	-
P	<10	<10	<10	<10	<10	<10	10	<10	<10	<10	<10	<10	16	<1

* Number not included in calculated average.

+ Averages for Al, B, Fe, and P include sample numbers 67 through 628.

APPENDIX A3. IMPURITY ANALYSES OF ARKANSAS MILKY QUARTZ

Impurity (ppmw)	Sample Number														Average
	89	92	110	111	112	113	114	115	122	123	124	125	126	127	
Al	10	10	10	40	10	20	70	<10	60	20	10	<10	30	40	20
B	<1	<1	<1	<1	<1	<1	<1	<1	2	2	1	1	2	1	1
Ca	<10	<10	<10	<10	<10	<10	<10	<10	20	<10	<10	<10	<10	<10	<10
Cr	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cu	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Fe	10	10	10	20	20	30	30	10	20	30	20	60	40	30	20
Mg	<5	<5	<5	6	<5	<5	6	<5	6	<5	<5	<5	<5	<5	<5
Mn	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ni	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
P	<10	<10	<5	<5	<5	<5	6	<5	<10	<10	<10	<10	<10	<10	<10
Ti	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
V	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zr	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

APPENDIX A4. IMPURITY ANALYSES OF BRITISH COLUMBIA QUARTZ

Impurity (ppmw)	Sample Number																
	256	257	258	282	298	299	300	301	302	487	488	547	548	609	619	620	630
Al	20	30	20	30	10	20	30	40	40	<10	<10	20	30	-	15	8	-
B	<1	<1	<1	5	5	4	6	6	6	<1	<1	<1	<1	2	<1	<1	<1
Fe	20	10	<10	<10	<10	<10	<10	<10	<10	10	10	<10	<10	-	<5	<5	-
P	2	4	<2	<10	<10	<10	20	<10	<10	<10	<10	<10	<10	2	<10	<10	<1

Impurity (ppmw)	Sample No.		Average*
	128	129	
Al	10	20	20
B	<1	<1	2
Ca	<10	<10	<10
Cr	<10	<10	<10
Cu	<5	<5	<5
Fe	30	<10	5
Mg	<5	<5	<5
Mn	<10	<10	<10
Ni	<10	<10	<10
P	<10	<10	2
Ti	<10	<10	<10
V	<10	<10	<10
Zr	<10	<10	<10

* Averages for Al, B, Fe and P include sample numbers 128 through 630 (see text for discussion).

**APPENDIX B. ANALYSES OF ACTIVATED CARBON SAMPLES THAT
DO NOT MEET PURITY GOALS**

Impurity (ppmw)	Carbon Goal	Sample Number								
		AC1	AC2	AC4	AC5	AC6	AC7	AC8	AC13	AC14
Al	100	180	170	50	40	50	1200	100	720	580
B	1	<5	<5	8	<5	<5	<5	13	8	<5
Ca	1000	120	210	1100	1000	1100	980	350	590	230
Cr	1000	<10	<10	<10	<10	<10	<10	<10	20	30
Cu	1000	10	<5	<5	<5	<5	20	20	72	65
Fe	1000	270	290	120	40	100	730	60	1200	780
Mn	600	10	20	80	70	80	40	<10	50	160
Mo	2000	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ni	1000	<10	<10	<10	<10	<10	20	<10	30	30
P	10	40	40	150	80	90	<10	190	320	90
Ti	70	10	30	<10	<10	<10	520	<10	190	330
V	50	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zr	1500	<10	<10	<10	<10	<10	40	<10	10	40

AC1: ICI Americas, Darco DXL-0-6839

AC2: DXL-0-6940

AC4: DXL-0-6878

AC5: DXL-0-6879

AC6: DXL-0-6880

AC7: DXL-0-4690

AC8: Calgon

AC13: Union Carbide, Columbia Coconut Charcoal

AC14: Acid washed AC13

**APPENDIX C. CROSS REFERENCE OF CARBON BLACK SAMPLE
NUMBERS WITH SUPPLIERS OF MATERIALS**

<u>Sample Number</u>	<u>Supplier</u>	<u>Trade Name</u>
CB1	Cabot Corp.	Monarch 700
CB2	Cabot Corp.	Monarch 1300
CB3	Cabot Corp.	Elftex 8
CB4	Cabot Corp.	Elftex 12
CB5	IMC	Thermax Stainless
CB6	Cabot Corp.	Vulcan 3H
CB7	Cabot Corp.	Vulcan 6-LM
CB8	Cabot Corp.	Sterling NS-1
CB9	Cabot Corp.	Mogul-L
CB10	Cities Service	Statex SL-4670
CB11	Cities Service	Raven SL-4701
CB12	Cabot Corp.	Sterling R
CB13	Continental Carbon	Continex N375
CB14	Continental Carbon	Continex N234
CB15	Continental Carbon	Continex N326
CB16	Continental Carbon	Continex N650
CB17	Schwanigan Chemical	
CB18	Philips Chemical	Philblack N110
CB19	Philips Chemical	Philblack N660
CB20	Cabot Corp.	Regal 660 R
CB21	Cabot Corp.	Sterling NS
CB22	Cabot Corp.	CSX 133